The Surface Tension of Molten Slags.

Thesis

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Doctor of Philosophy

by

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Contents.

Part I.

Introduction.

Surface tension is one of the direct manifestations of interatomic forces that can be readily and simply recognised and measured. In a solid the mechanical properties are an obvious guide to the strength of the bonding forces between the molecules, though the relationship is not quite so simple as was once believed. Though a liquid does not possess elasticity, its viscosity is indicative of a resistance to shearing forces. The surface tension, however, is directly related to the strength of the intermolecular bonds.

In some cases the surface tension can provide a clue as to the type and strength of bonding between the molecules, e.g. the powerful ionic bond is reflected in the high surface tension of fused salts. Molten metals also show high surface tensions, as would be expected from the nature of the metallic bond, while the surface tension of most organic liquids is very low, due to the weak Van der Waals forces which hold the molecules together.

In a series of substances which have the same type

of bond the surface tension is an indication of the strength of the bond.

	F	Cl	Br	I	
Li	237	110	-	-	dynes/cm.
Na	200	100	89	70	dynes/cm.
K	132	81	70	58	dynes/cm.
Rb	107	74	69	56	dynes/cm.
Cs	83	65	60	53	dynes/cm.

The surface tensions of the above halides[1] vary in the same manner as the bond strengths determined by the anion sizes.

In most cases the surface tension is not the best method of investigating the intermolecular bonding and hence the constitution of substances[2]. In liquid slags, however, the surface tension can be a valuable confirmation of a constitution which has been predicted from other considerations, e.g. the structure of the solid, as determined by X-ray work and the modifications of this structure as indicated in the liquid by density and viscosity measurements.

The structure of liquid slags is of importance in leading to a better understanding of their functions in

process metallurgy. Interest in this structure has grown with the development of the thermodynamic approach to slag-metal reactions. In some instances a structural model is an aid to the correct interpretation of the reactions. Richardson has indicated this in a discussion of the present state of knowledge of liquid slag structures[3].

In the present research attention has been focussed on the structural interpretation of the results.

According to Bikerman[2] the surface tension in binary and more complex systems is not a good indication of the presence of certain phases. Often the surface tension varies in a regular manner between two components in a binary system with no indication of compound formation. Surface activity is, however, easily recognisable and may often be of importance. As an example of this, Kozakevitch[4] has found Na_2O and P_2O_5 to be surface active with respect to FeO and presumably, iron silicate slags. Interfacial reactions involving these components are likely to have different rates of approach to equilibrium than those expected from the volume concentrations.

While the structural interpretation is possibly

the most interesting aspect of the surface tension of slags, other phenomena involve surface tension directly or indirectly. Slag attack on refractories has been shown to depend as much on the porosity of the refractory as on the chemical nature of slag and brick. It is therefore a problem of penetration of slag into pores, by which a much larger reacting interface is made available. If the slag wets the brick, then the force driving slag into capillary pores is larger the larger the surface tension of the slag and the smaller the contact angle between slag and brick. If the angle of contact is greater than 90° then, of course, the force due to surface tension is directed so that the slag tends to be pressed out of the pores. This is probably the reason for the low reactivity with slags of carbon blocks, observed in blast furnace hearth walls. Reaction is very slow, even with oxidising slags, as is sometimes noted in laboratory work with carbon crucibles. A correlation between attack and surface tension might be difficult since the contact angle is likely to exert a bigger influence than the surface tension and the difficulties involved in measuring contact angles between slag and refractory are enormous. The upward drilling of glass tank

refractories is an example of the same phenomenon which has been investigated from this viewpoint, though without much success[5].

Into the same field comes the problem of the formation of slags in the blast furnace and their subsequent penetration through a mass of coke to the hearth of the furnace. The porosity of the coke bed just above the tuyeres is not of the capillary type with coke of 2 ins. or so in size. Hence, the slag is more liable to penetrate quickly as droplets if it can run down without wetting the coke surface.

Variations in furnace working with regard to hearth heat and slag composition which cannot be explained by viscosity or melting point variations in the slag may be due to changes in contact angle between slag and coke with change of slag composition[6]. The surface tension value is probably of lesser importance here than the contact angle.

In reactions at the interface between slag and metal, e.g. in the open-hearth furnace, another effect of surface tension is apparent when the reaction gives a gaseous product. It is not sufficient to assume that the equilibrium is determined by the pressure of the gas e.g. p_{CO} in the

reaction $FeO + C \rightleftharpoons Fe + CO$. The equilibrium may tend to lie to the left side, and the rate of reaction will certainly be altered, by the difficulty of forming gas bubbles and their subsequent rise through the interface to the slag surface. Entrapment of bubbles at the interface reduces the contact area available for reaction and hence may slow up the reaction considerably. The interfacial tension between liquid steel and slag is the determining factor here. If it is large then the bubbles will tend to remain small and spherical; if small, they tend to become lenticular and occupy more of the interfacial area. Unfortunately predictions of the interfacial tension from the component surface tensions are difficult unless the contact angle between the liquids is known, a quantity very difficult to measure even on substances which are liquid at room temperature.

Foaming of open hearth slags, especially acid slags, when the carbon is being eliminated, has remained a problem with no easy solution. The foaming tendency cannot be correlated with the slag viscosity or the presence of solid particles in slag, and it would seem that a connection between froth stability and the surface tension of the slag must exist. Such a connection remains obscure even in aqueous solutions of surface active substances which have

been investigated very completely[7] though it is conceded that the variation of surface tension with composition must be fairly sharp, i.e. the dissolved substance should be truly surface active. Other factors, e.g. surface viscosity, play a part. It should be possible from the surface tension of slags and its variation with composition to determine whether frothing slags do contain a surface active constituent. Kozakevitch[8] has suggested an explanation of this nature which coincides with a widely held view that silica enrichment on the surface is a possible cause of frothing; the high viscosity of a surface layer rich in silica would then tend to stabilise a froth.

The coalescence of inclusions and their subsequent rise to the surface of metal which is being held in a ladle has often been termed one of the phenomena which depend on surface tension, high surface tension favouring coalescence. It is difficult to see why surface tension should have any effect on coalescence unless the separate inclusions are by chance brought very near to each other, in fact, touching. Then, any surface tension at all should ensure their coalescence.

The present work was undertaken with two objects in view.

1. The development of a suitable apparatus which would give reliable, and preferably absolute values of the surface tension of slags at temperatures up to 1600°C.

2. The use of the surface tension values obtained, in conjunction with known values of viscosity, in deciding some features of liquid slag structures, e.g. the presence of compounds in the liquid phase. It was hoped that the results might also give some indication of why certain slags are subject to foaming.

Part II.

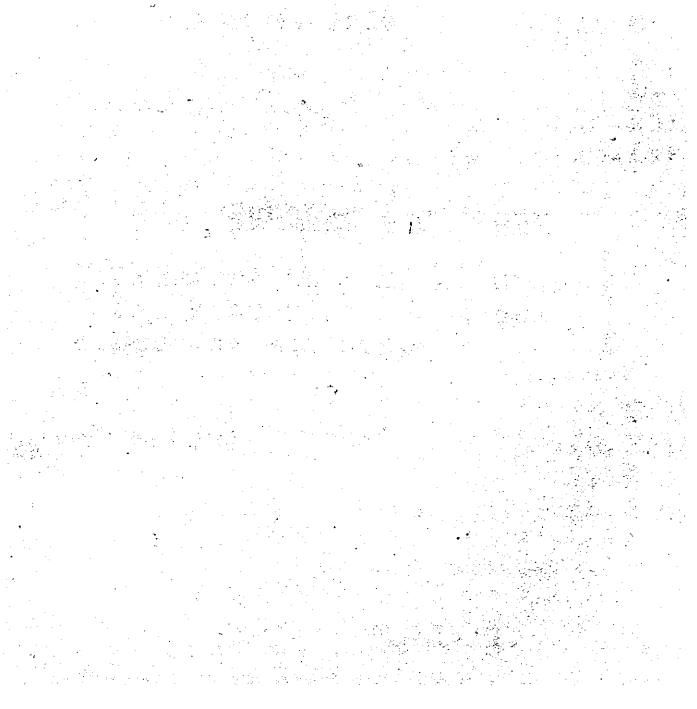
Measurement of Surface Tension.

The tendency for the free surface of a liquid to assume a shape having minimum area, as exemplified in the shape of bubbles and drops, is explained by postulating a tension in the surface which causes it to contract like an elastic skin. The surface has, however, no modulus of elasticity; a new surface is created by stretching.

Another way of explaining capillary phenomena is to attribute to the liquid surface a free energy. Extension of the surface area then requires work which can be given up by the surface if it is later allowed to contract. The dimensions of the free surface energy are energy/area or ergs./cm^2 or gms./sec^2. This can also be expressed as dynes/cm. or force/length. Hence the conception of a "surface tension", numerically equal to the surface energy. The surface tension generally decreases continuously with increase in temperature since it must vanish just before the critical temperature.

The origin of surface tension lies in the unbalanced molecular forces which must exist at a liquid surface bounded by a gas. A molecule on the surface is attracted only towards the interior of the liquid; therefore expansion of the surface area requires work to be done against the intermolecular forces. This is the basis of the Laplace view of capillary forces. Since intermolecular forces are

regarded as independent of temperature it is not surprising to find that the relation between the temperature coefficient of surface tension and the coefficient of thermal expansion is such that the decrease in surface tension can be regarded as due entirely to the thermal expansion.



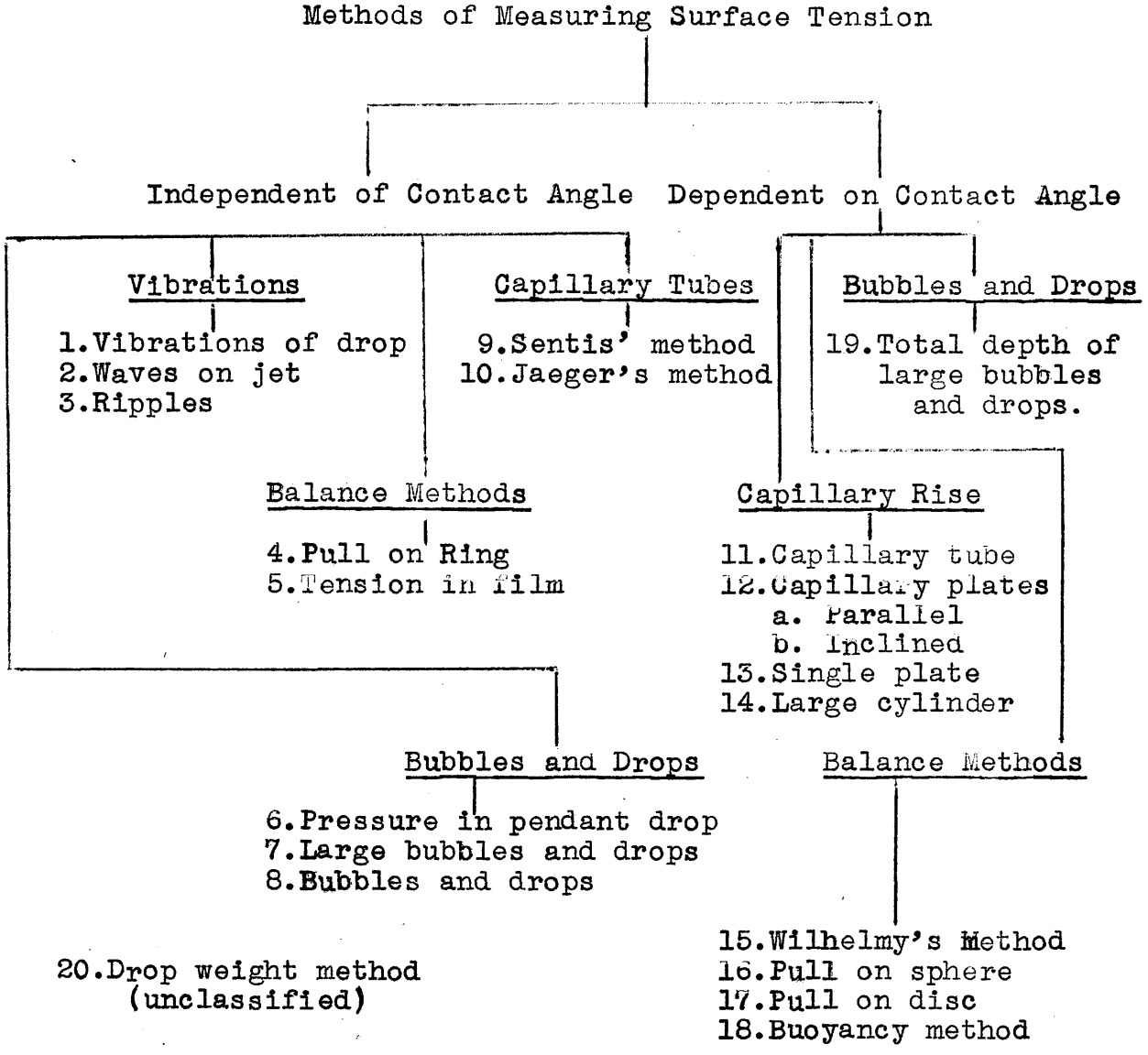

Methods of Measuring Surface Tension
Independent of Contact Angle
Dependent on Contact Angle
Vibrations
1.Vibrations of drop
2.Waves on jet
3.Ripples
Capillary Tubes
9.Sentis' method
10.Jaeger's method
Bubbles and Drops
19.Total depth of large bubbles and drops.
Balance Methods
4.Pull on Ring
5.Tension in film
Capillary Rise
11.Capillary tube
12.Capillary plates
a. Parallel
b. Inclined
13.Single plate
14.Large cylinder
Bubbles and Drops
6.Pressure in pendant drop
7.Large bubbles and drops
8.Bubbles and drops
Balance Methods
15.Wilhelmy's Method
16.Pull on sphere
17.Pull on disc
18.Buoyancy method
20.Drop weight method (unclassified)

Table 1.

Methods of measuring surface tension may be classified according to Table 1. due to Ferguson$_{10}$. Fundamentally, they may be classified according to the capillary phenomena which are employed. The methods of sessile and pendant drops and bubbles and that of maximum bubble pressure may be grouped together as methods dependent on the pressure difference at a curved surface.

In the Laplace equation,

$$P = \left(\frac{1}{R_1} + \frac{1}{R_2}\right)$$

where P = capillary pressure

R_1 and R_2 = principal radii of curvature of surface.

Into this class comes the capillary rise method but the relevant equation $h = 2\gamma/r\rho g$ can also be derived without invoking capillary pressure. (Note. γ =surface tension, ρ =density, throughout.)

All capillary pull methods, such as pull on plates, wire rings or frames etc., depend on the surface tension; capillary pressure is not necessary in the derivation of the appropriate equations.

The pull on a plate, for example, is given by $L\gamma\cos\theta$, where L is the perimeter of the plate and θ is the angle of contact.

While all these methods are quite satisfactory for use with mobile liquids at room temperature, the measurement of surface tension of slags presents several problems.

The choice of a suitable method of measuring surface tension was tempered by three considerations.

1. The method must be, if not absolute, at least not completely empirical, since little is known of slag surface tensions.
2. It must be adaptable to use at high temperatures.
3. It should be quickly and easily carried out on a reasonably small sample.

The second consideration has proved to be the controlling factor. It rules out the only method which has been analysed to complete satisfaction, that of capillary rise, since the visual observation of height of rise is impossible with slags which can only be contained in platinum or iron capillary tubes and crucibles. It might be possible to use X-rays for observation but this is a considerable complication.

The methods of pendant drop and sessile drop can

be carried out in a horizontal furnace[11] but are most unreliable and have not been well analysed.

Of the other methods listed in Table 1. , only the maximum bubble pressure and detachment methods are worthy of further consideration. The former has been fairly well analysed and Sugden's treatment [12] renders it very accurate. It has been used successfully by Jaeger[13] and others on room temperature liquids. Its use at high temperatures is subject to a few criticisms. The first of these is the doubt that exists about the conditions of detachment of bubbles from a tube which is not perfectly shaped; this is more difficult to ensure with platinum than with glass[14]. Other minor drawbacks are that it demands a certain depth of slag and therefore a reasonable slag bulk. This has been found to be a serious limitation. Cleaning crucibles is more difficult when they are of deep section and is a lengthy process even with shallow basins. Since some of the slags which were to be investigated are subject to foaming it was felt that this might prove a possible source of trouble. There is probably little to choose between the methods of bubble pressure and detachment of rings but the latter has been better analysed and permits of an apparatus as simple as the former.

Detachment methods have been used by many workers, especially in studies of capillary active substances and spreading.

A ring has been the favourite choice, though Lenard[15] used a frame and others, e.g. Abribat and Dognon[16], have used a plate. The ring is convenient and has been made an absolute method by the work of Freud and Freud [17]. They have analysed the shape of the liquid surface supported by a ring and given a method of calculating the surface tension from measurements of the maximum weight of liquid supported by the ring and the dimensions of the ring itself. The method is therefore intrinsically accurate, involving measurements of mass and length, both of which can be made more precisely than is probably necessary.

It has been successfully used by several workers but few measurements have been made above 1450°C.

While the ring method has been used to obtain all the results in the present investigation doubts were felt at first about the ability of a ring (or even a hollow cylinder) to maintain its shape and remain in a horizontal plane at high temperatures. Tilting of the ring introduces

a considerable source of error[18]. These doubts have since proved unfounded but a preliminary investigation was conducted using a sphere as the detachable body[19]. The advantage of a sphere is that the shape presented to the liquid surface is the same irrespective of whether the sphere tilts. The analysis of the shape of the liquid surface drawn up by a sphere is difficult. Ferguson[20] has considered the problem and developed an expression from which the surface tension can be calculated from the radius of the sphere and the excess weight when the sphere just touches the liquid surface. This solution to the general differential equation is, however, valid only when the sphere is at least 14 cms. in diameter, i.e. its radius is large compared with the vertical radius of curvature of the liquid surface. A more accurate, though more complex solution contains terms in "d", the height of the liquid surface, at the point of contact with the sphere, above the general level. With spheres of the size that could be used at high temperatures where the furnace diameter is the limiting factor, Ferguson's solution was shown to give erroneous results and a technique of measuring d by measurement of the height of the solid skin remaining on the sphere when removed rapidly from the furnace was developed. The method thereby becomes

less accurate and much more inconvenient but it was used to obtain some results on a manganese silicate of composition $MnO.SiO_2$. These showed that the surface tension increased with temperature up to about 1535°C. and then decreased, thus showing a maximum.

This result has not been confirmed in the present work. The value of surface tension is of the same order but the temperature coefficient is small and remains positive over the range 1450°C. to 1600°C. It has since been proved that the previous results were fortuitous and that it was possible to obtain either high or low readings at the same temperature because of a fault in the apparatus. The sphere used was of platinum, cast from scrap and turned to a hemisphere over the lower surface. The forming technique left a ridge slightly above the hemisphere and the higher readings were due to allowing the sphere to be drawn too far into the slag when contact was made. The liquid raised was then attached at the ridge which was of greater perimiter than the body of the sphere. This fault could be eradicated quite simply but it was not foreseen that the slag could rise to the level of the ridge, an effect only possible with liquids which have a high ratio of surface tension to density.

Since an absolute method is always to be preferred, the sphere was abandoned in favour of the ring. The desirable rigidity at high temperatures was attained by using a thin-walled cylinder with an accurately-cut edge instead of a wire ring. The cylinder is thus equivalent to a ring of rectangular cross-section.

Previous high-temperature work.

The volume of previous work on surface tension is considerable but relatively few measurements have been made above 1000°C. Experimenters have favoured two methods for use at high temperatures, the maximum bubble pressure method and one of the modifications of the ring method. The first of these has been used by Jaeger[1] on molten salts up to 1650°C., by Badger, Parmelee and Williams [21] (among others) on molten glasses and by Bircumshaw [22] and Saeurwald [23] on molten metals and alloys. The ring method has been adapted to work on molten glasses by Washburn&Libman[24], Babcock[5] and Silverman[25] all of whom determined the maximum pull. Kozakevich[4] has also used the ring method for determinations on molten slags, containing iron oxide. A third method in which a suspended fibre of the material is heated at various points along its length until its weight just balances the pull of

surface tension has been used by some workers. The method, which is not accurate, is due to Tamman[26].

The work of Babcock[5] is typical of that on glasses and a short resumé of his method is of interest. He used a 3 inch. diameter platinum-rhodium resistance furnace. A platinum-rhodium basin, placed on a stool which could be moved up and down within the furnace, held the glass, while a cylinder of platinum-rhodium (1 ins. diameter x $\frac{3}{4}$ ins. high) was suspended from an accurate spring balance. The maximum pull was measured by alternate lowering of the crucible and setting the balance to its zero position. The method is then very similar to that used in the present investigation.

Babcock claims an accuracy of $\pm$ 1 dyne/cm. i.e. about 0.6%, but from the dimensions of the cylinder used it would seem that the corrections of Harkins and Hordan[18] are necessary to give absolute accuracy. Measurements were made on a series of glasses from which factors for calculation of surface tension could be derived. It is of interest that the viscosities of the glasses were over 1000 poises; in the present work it has been found to be difficult to attain reasonably accurate results on liquids with viscosities of more than about 20 poises. All the glasses measured had

negative temperature coefficients of surface tension.

Harrison and Moore [27] working with glasses, and Kozakevitch[4] working with slags, used a method similar to that of Babcock except that the pull was measured when the bottom of the cylinder was coincident with the general level of the liquid. It is likely that the contact angle has a much bigger effect on the result than when the maximum pull is measured. There is also the criticism that the method, used in this way, no longer gives absolute results.

The work of Kozakevitch[4] is of special interest since it represents the only known determinations of surface tension carried out on typical slag minerals. His apparatus consisted of a carbon-granule type furnace equipped with a cam arrangement for raising and lowering. The platinum cylinder was attached to a steelyard type balance, bearing a scale at one end which is observed through a telescope. The balance could be raised mechanically to remove the cylinder from the furnace altogether. A platinum cylinder, though attacked by slags containing iron oxide, had to be used, since, with an iron cylinder, the surface layer of slag in contact with the cylinder is substantially FeO. An iron crucible was employed since

the furnace atmosphere was slightly reducing. Measurements of surface tension were made on different slags at only one temperature, between 1400°C. and 1450°C., so that nothing is recorded about the change of surface tension with temperature. Results are given for a series of additions to FeO, viz., SiO_2 up to 26 mol.%, CaO to 26 mol.%, TiO_2 up to 20 mol.%, MnO up to 10 mol.%; Al_2O_3 up to 5 mol.%, Na_2O up to 8 mol.% and P_2O_5 up to 5 mol.%. The FeO rich corners of the ternary systems FeO - CaO - SiO_2; FeO - MnO - SiO_2 and FeO - Na_2O - SiO_2 were also covered. Values of surface tension vary from 585 dynes/cm. for FeO to 405 dynes/cm. for FeO containing 5 mol.% P_2O_5. Kozakevitch claims an accuracy of 1 or 2% which represents 5 or 10 dynes/cm. but the error is thought to be mainly in the presence of 5% Fe_2O_3 in the slags, uncertainties in the analyses of slags, etc. It was noted that all slags wet platinum very well so that the contact angle should not have much influence on the results. Only Al_2O_3 was found to raise the surface tension of FeO. Of the other oxides, Na_2O and P_2O_5 are surface active with respect to FeO. As mentioned in PartVIII Kozakevitch believed silica enrichment on the slag surface to be responsible for the stability of foams. It is also concluded that the raising of surface tension by lime additions to FeO; CaO; SiO_2 slags

is due to removal of silica from the surface layer to form inactive calcium silicates. This is hardly likely according to present views of the structure of liquid slags (see Part VI.). Kozakevitch's results do, however represent a remarkable amount of work extending over a long period and are, at present, the only contribution to the literature on the surface tension of slags.

Part III.

Theory of Ring Method.

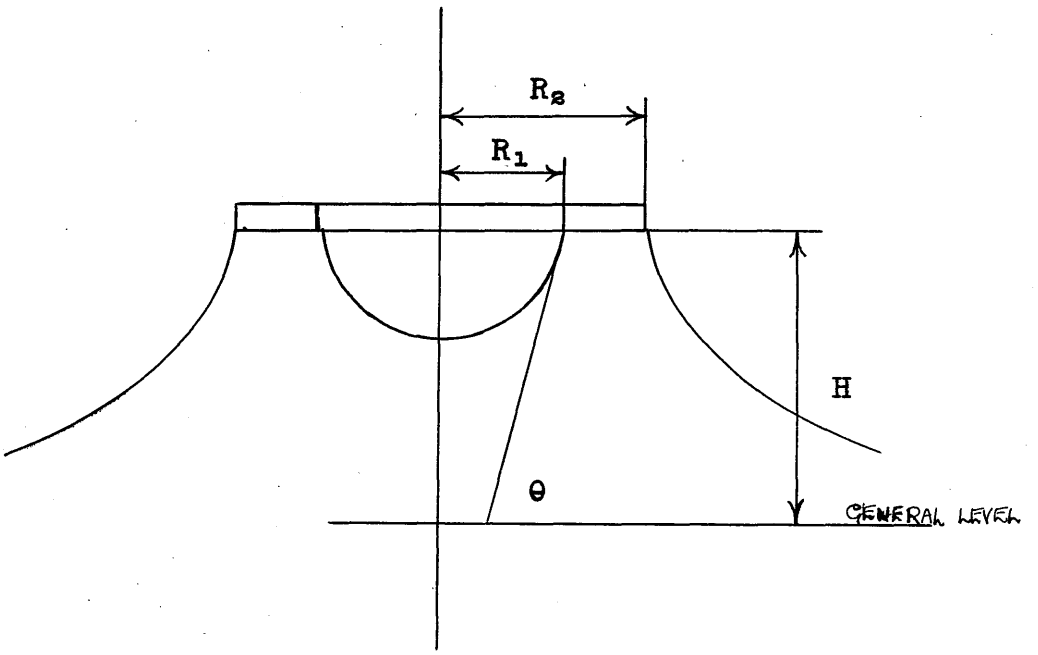


Fig. 1.

Attachment of liquid to ring.

Theory of Ring Method.

In spite of the numerous investigations which have been conducted with the ring method, confusion still exists regarding the correct analysis of the problem. Too often it is assumed that a very simple formula may be used.

The following treatment is taken from Champion and Davy[28]. If the ring be suspended horizontally, dipped into the liquid and then raised, the downward pull on the ring reaches a maximum before the attached column of liquid breaks. This maximum is the quantity generally measured. The ring is flat so that the difficulty of determining the point of attachment of the liquid on a circular cross-section is avoided. This treatment suffices also for the cylinder used in the present investigation. Fig. 1 shows the ring partly lifted from the liquid surface and it is assumed that the inner and outer liquid surfaces meet the ring at the same angle θ. The pull on the ring is calculated as follows:-

Downward pull due to surface tension $= 2\pi(R_1 + R_2)\, T \sin\theta$

Downward force on face of ring $= P\pi(R_2^2 - R_1^2)$

Upward force due to liquid pressure $= \pi(R_2^2 - R_1^2)(P - g\rho H)$

(P=atmospheric pressure.)

Total downward force (m) (in addition to weight of ring)

$$= 2\pi(R_1 + R_2)\, T \sin\theta + \pi g \rho H\, (R_2^2 - R_1^2) \text{ dynes} \quad ---(1)$$

The normal procedure is to assume that the maximum pull occurs when $\theta = 90°$. Then, if R_1 and R_2 are nearly equal,

$$m = 4\pi RT \qquad \text{where } R = \frac{R_1 + R_2}{2}$$

Difficulties are associated with calculation of the maximum pull when these assumptions are not made since m varies with θ and also with H. In related problems the substitution $g\rho H^2 = 2T(1-\cos\theta)$ may be made. This is the equation to the capillary curve of a liquid against an infinitely long inclined plate. The substitution is valid therefore only when the curvature of the liquid surfaces is very large in one dimension i.e., in this case, when the ring is very large. This is not the case in most work using the ring method. The two radii of curvature of the liquid surfaces are, in fact, comparable with each other for the cylinder used in the present investigation.

Even with the simplification that the ring is of very thin material compared with its radius i.e. $R_1 \doteqdot R_2$, the expression still presents difficulties. We have $m = 4\pi RT \sin\theta$. The maximum value of m is reached when $\theta = 90°$. This is often taken to mean that for liquids of

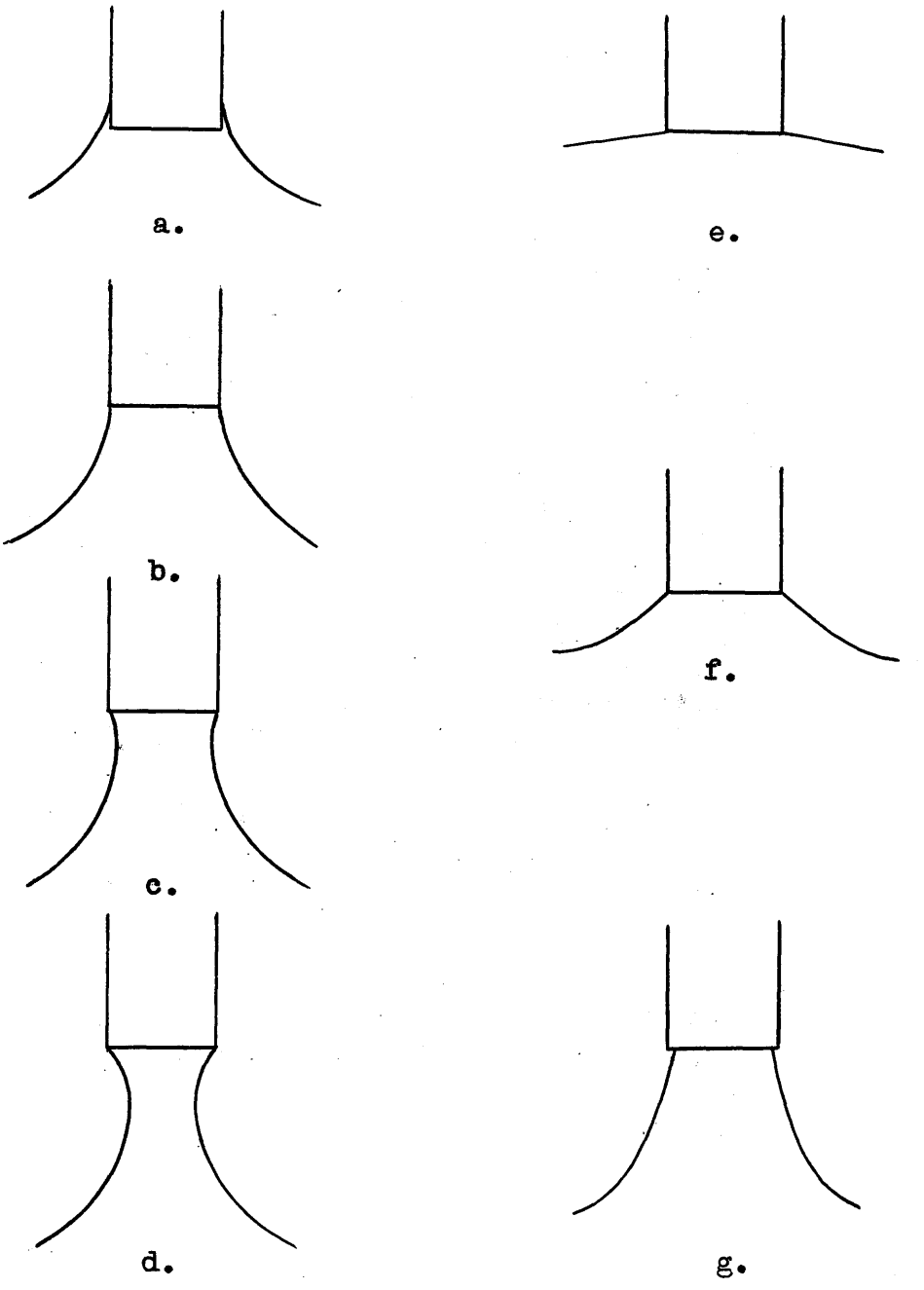


Fig. 2.

Shape of liquid surfaces in contact with cylinder as cylinder is raised. (c.) and (g.) are the positions of maximum pull.

zero contact angle, the simple expression $m = 4\pi RT$ will suffice. θ however, is not necessarily the contact angle between ring and liquid. The use of the simple expression for liquids of zero contact angle then implies that the maximum pull is reached when the surface tension force is acting vertically downwards i.e. when the liquid surfaces meet the ring so that the tangents to the profile curves are vertical.

Experiments have been conducted using water and benzene, for which the contact angle against platinum is very nearly zero, and observing the shape of the outer liquid surface at various stages during the raising of a cylinder to the position of maximum pull (see Fig. 2.). It is clear from these experiments that the liquid surface has a considerable curvature where it contacts the cylinder such that the surface tension force is not acting vertically downwards when the cylinder is in the position of maximum pull. This observation is verified by the work of Hauser, Edgerton, Holt and Cox[28] who studied the detachment of a ring by means of high-speed cinematograph technique.

It would seem therefore that, even with rings or cylinders of very thin material such as the one used in the above experiments, the second term of equation (1)

cannot be neglected, otherwise the maximum pull would be reached when the surface tension force was acting vertically downwards. The inner meniscus is difficult to observe but, even at the position of maximum pull, when the outer liquid surface contacts the cylinder along an edge, the inner meniscus still contacts the cylinder on a vertical surface. For liquids of zero contact angle then, the conditions implied by the simple equation $m = 4\pi RT$ apply only to the inner liquid surface.

Consideration of equation (1) in conjunction with the experiments outlined above make it clear that the pull on a ring of rectangular section depends on:-

(1) The dimensions of the ring itself.

(2) The shape of the liquid surfaces in contact with the ring. This is determined by the surface tension and density of the liquid and the contact angle between ring and liquid.

Harkins, Young and Cheng[30], and Harkins and Jordan[18] in an investigation of the factors governing the ring method concluded that the simple formula $m = 4\pi RT$ could give results as much as 30% in error. They used only rings of circular cross-section and assumed that the correct value

was given by $F.m = 4\pi RT$ where F is a non-dimensional factor. F was assumed to depend on $\frac{R}{r}$ the ratio of the mean radius of the ring to the radius of the wire used and also on $\frac{R^3}{V}$ where $V = \frac{m}{\rho g}$ = volume of liquid held up by the ring. Using water, benzene and bromobenzene, liquids of zero contact angle with platinum, they measured the maximum pull on several rings with different R and r.

They plotted the results on graphs with abscissae $\frac{R^3}{V}$ and ordinates $\frac{\gamma}{p}$ where $p = \frac{m}{4\pi R}$. The values of γ, the true surface tension, were obtained by the capillary rise method. A family of curves with different $\frac{R}{r}$ values could be drawn through the points thus obtained. From these, correction factors for the ring method were calculated so that, if $\frac{R}{r}$ and $\frac{R^3}{V}$ be measured for the ring used in any investigation, the factor for calculation of the true surface tension can be obtained. A contact angle of zero is, of course, assumed. One of the greatest sources of error was found to be tilting of the ring: for small angles of tilt the error in m was proportional to the square of the angle. Though this procedure is semi-empirical the value of the correction factors is enhanced by the work of Freud and Freud[17] who have evolved a correct mathematical analysis of the problem. A graphical solution of their equations is necessary but

they have confirmed that the factors of Harkins and Jordan give results which agree almost exactly with those calculated from their treatment. The ring method has, therefore, an absolute basis but, practically, there is nothing to be gained by preferring the theoretical treatment to that of Harkins and Jordan.

Other attempts have been made to derive a more accurate expression from which to calculate the surface tension. Verschaffelt[31] used the following expression for a ring of rectangular section when $\theta = 0$.

$$T = \frac{F}{4\pi R}\left[1 - \left(2.8284 + 0.6095\sqrt{\frac{h}{R}}\right)\frac{\delta}{\sqrt{hR}} + \left(3 + 2.585\sqrt{\frac{h}{R}} + 0.371\,\frac{h}{R}\right)\frac{\delta^2}{Rh}\right]$$

where $h = \frac{F}{\pi R^2 \rho g}$, R = mean radius of ring, $\rho = \rho_2 - \rho_1$, 2δ = vertical thickness of ring

The complication involved is probably, in part, unnecessary and there seems little point in the use of such formulae when the corrections of Harkins and Jordan have a sound, theoretical basis.

The relation between the maximum pull as measured by a ring of circular cross-section, such as those used by Harkins and Jordan[18] and a cylinder, such as is used in the present work, is not at all obvious. The treatment of

Freud and Freud[17] is applicable to both cases but the graphical solution of their equation is not reproduced in enough detail to enable a direct comparison to be made for the two types. The most obvious difference is that with liquids of zero contact angle the liquid meniscus and outer surfaces will always meet a ring of circular section tangentially. Variation in the angle between this tangent and the vertical must be brought about by movement of the point of attachment round the surface of the ring. With the cylinder however, or with a ring of rectangular cross-section, variation in the angle between the line of action of the surface tension pull and the vertical is only possible when the outer liquid surface meets the cylinder at the edge (see p.24.). This conclusion is supported by Freud and Freud who treat the ring of square cross-section as a problem of two shapes, the shape of the outer liquid surface, which is that attached to a flat circular disc, and the shape of the inner surface, which is a meniscus, as in capillary-rise experiments. The first problem is capable of accurate solution only if the disc be large. According to Ferguson[20] uncertainty exists as to the angle at which a liquid meets a disc along an edge. The observations reported on p.24. show that this is not the angle of contact along either

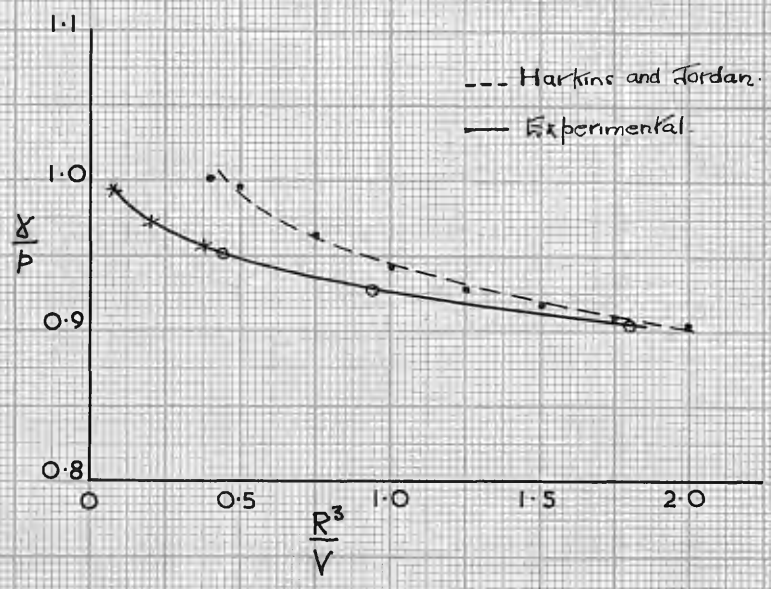


Fig. 3.

Variation of γ/ρ with R^3/V.

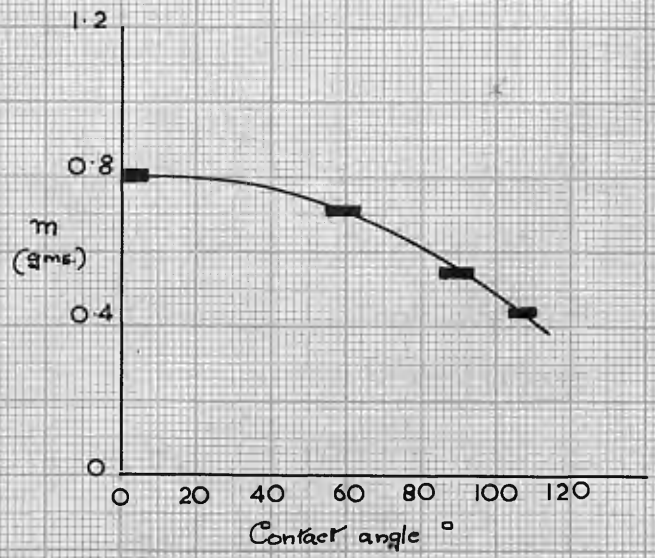


Fig. 4.

Variation of maximum pull (m) with contact angle.

the vertical side or the bottom face of the disc.

In view of the differences outlined above between rings of circular section and cylinders it was deemed advisable to repeat the work of Harkins and Jordan using the platinum cylinder. The maximum pull, p, was determined for three liquids, pure, conductivity water, benzene and carbon tetrachloride. The surface tension, γ, of these liquids is well-known but the actual samples were checked by the capillary-rise method. Values of $\frac{\gamma}{p}$ and $\frac{R^3}{V}$ were calculated. Water gives the lowest value of $\frac{R^3}{V}$ of all normal liquids because of its high surface tension to density ratio. A small brass cylinder with the same ratio of $\frac{D}{d}$ (= 87.0) was used to obtain values of $\frac{\gamma}{p}$ at still lower values of $\frac{R^3}{V}$. It was lightly etched with acid to ensure zero contact angles. Harkins and Jordan[18] do not quote corrections for values of $\frac{D}{d}$ over 80 but the shape of their correction curves can be seen from the one for $\frac{D}{d}$ =60 which is plotted in Fig. 3 along with the curve determined as above. It is obvious that the factor $\frac{\gamma}{p}$ does not increase so rapidly with diminishing values of $\frac{R^3}{V}$ for the cylinder as it does for the ring. An exact comparison is not possible since the slope of the curve also falls off as $\frac{D}{d}$ increases.

Most slags have fairly low values of $\frac{R^3}{V}$ so that the correction becomes important since the slope of the curve is greatest here.

Ferguson[10] has listed the ring method as independent of contact angle. Theoretically this cannot be true, yet only one investigation as to the effect of contact angle has been carried out[32]. This showed that the maximum pull decreases as the contact angle increases , the effect being small with small contact angles. The effect also becomes less as the thickness of the ring decreases. It is difficult to give a precise relation between maximum pull and contact angle because of the uncertainty involved in measuring the contact angle.

Experiments of this nature have been carried out with the present apparatus since the previous workers used a ring of circular cross-section. The cylinder was coated with paraffin wax, Canada balsam, stearine wax and collodion in turn and the maximum pull measured for pure water. The contact angle was estimated by observation through a telescope of the outer surface when the cylinder first made contact - the mean of the advancing and receding angles was taken, though it should be noted that, in actual measurements, the receding angle is the one of importance, The resulting curve, fig.4, is similar to

that obtained by Nietz and Lambert[32]. Again it appears that the effect is small unless the contact angle is greater than 50° or 60°. An error of 1% is introduced by a contact angle of about 20°. It is, at first sight, surprising that a pull is observed even when the contact angle is greater than 90°. When the cylinder first touches the surface contact is being made on the vertical sides of the cylinder and, as expected, an upthrust is observed. When the cylinder is raised the liquid contacts it along the bottom edge (see Fig.2e.) and a pull can be observed. In this case the maximum pull position and the separation of the cylinder from the liquid practically coincide. No liquid remains on the cylinder showing that, as would be expected, the liquid slides cleanly off the bottom edge and does not break further down the raised column as is the case with small contact angles. The curve shown is lacking in points for angles between 0° and 60°. It seems difficult to obtain a coating which will show a medium contact angle with water and yet will not contaminate the surface, so altering the surface tension.

All the slags so far investigated wet the platinum cylinder fairly well - all show a residue on the cylinder after removal, though this residue is small

for some slags. It has been concluded therefore that the effect of contact angle is relatively small and no corrections have been made for it.

Part IV.

Experimental.

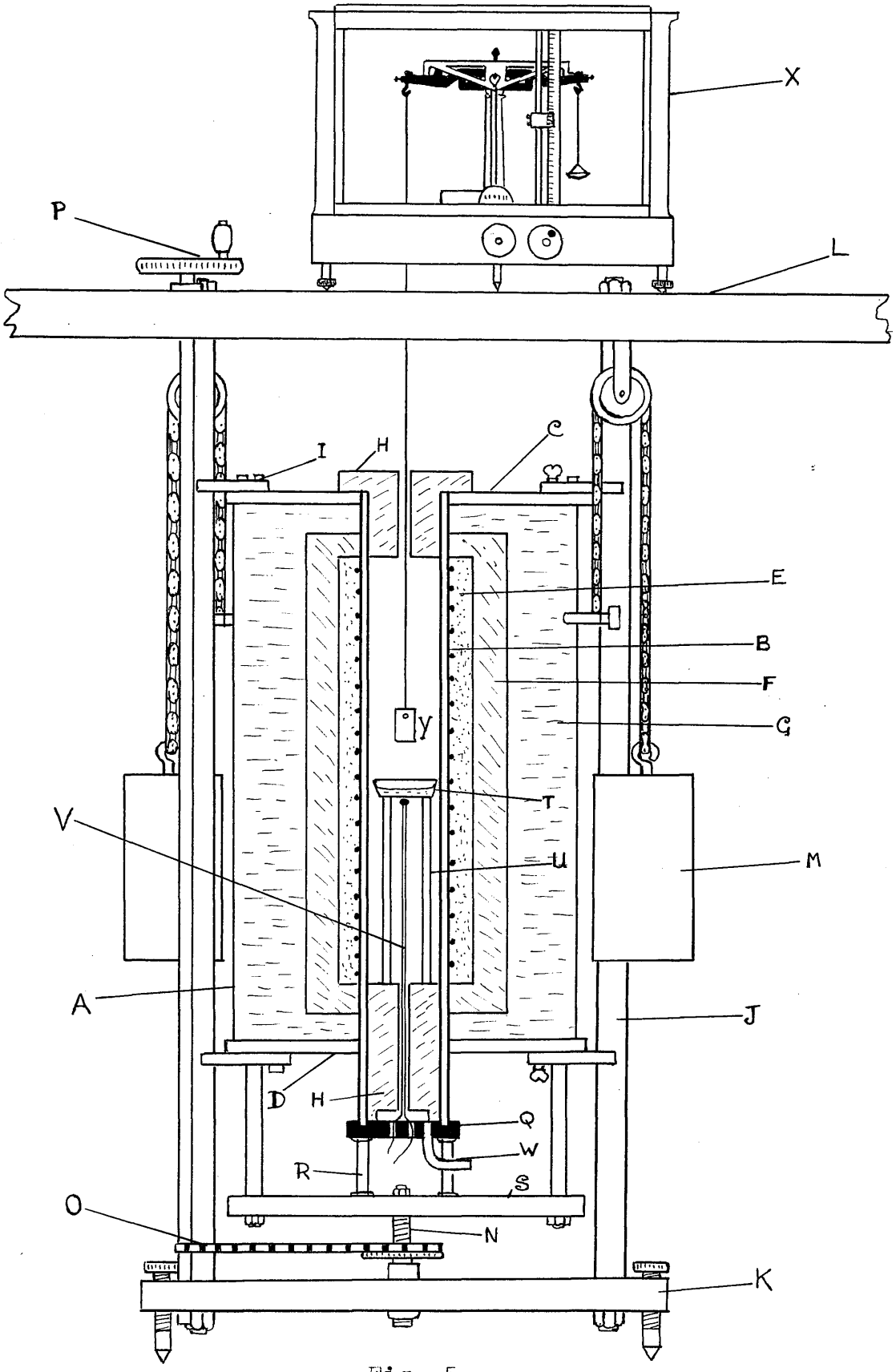


Fig. 5.
Apparatus

The apparatus developed is shown in Fig. 5 . It consists of a high temperature resistance furnace (A) with a 3.$\frac{1}{4}$ ins. internal diameter mullite (ΔH5) furnace tube (B). The winding, of 18 gauge platinum, 10% rhodium wire covers only 12 ins. of the 24 ins. length. It operates through controlling resistances on D.C. Grading of the winding has not been carried out as experience has shown that a sufficiently long hot zone, about 2 ins., can be obtained with an evenly-spaced winding and efficient, end insulation. The wire is wound directly on to the working tube which should mean that the wire temperature is only about 20°C. higher than the temperature inside the tube. Normal practice is to use a separate tube (of alumina) for the winding but higher temperatures are possible with the present arrangement. The furnace casing is 15 ins. external diameter x 18.$\frac{1}{2}$ ins. long, the mullite tube being flush with the top end cover (C) which is, like the bottom cover (D), of asbestos board. Insulation consists of 1.$\frac{3}{8}$ ins. of fused alumina powder (E) next to the winding, surrounded by 1.$\frac{1}{2}$ ins. of crushed insulating firebrick (F) and 3 ins. of diatomaceous brick (G). Since the winding only occupies 12 ins. of the length of the furnace the firebrick insulation is carried right in to the mullite tube above

and below the winding. End insulation of the tube is achieved by composite insulating plugs of porous alumina, insulating firebrick and diatomaceous brick (H). Such efficient insulation is necessary with a large diameter tube. The furnace is mounted so that it can slide on brass guides (I) between two vertical steel pillars (J) of 1 ins. section bolted to a cast iron base (K) and to the slate shelf (L) which is attached to wall brackets. This shelf takes part of the weight so that floor vibration has little effect on the furnace. Most of the weight of the furnace is counterbalanced by two cast iron weights (M) so that it can be raised and lowered by a single screw (N) operated by a chain drive (O) and handwheel (P) from the same level as the balance.

The bottom end of the furnace tube is sealed by a grooved plate (Q) with a greased rubber washer which is held against the ground end of the tube by two screwed pillars (R) attached to the cross-bar (S) which supports the furnace on the raising and lowering screw. This arrangement has proved more satisfactory than a rubber bung.

The crucible (T) for holding the slags is of platinum, 10% rhodium alloy 2.$\frac{7}{8}$ ins. external diameter, $\frac{3}{4}$ ins. deep and flat-bottomed, with tapered sides.

(An iron crucible (Armco) of similar dimensions was used for iron silicates.)

It is supported on a length of 2 ins. diameter mullite tube (U) which rests on the insulating plug. The platinum/13% rhodium, platinum thermocouple (V) just touches the bottom of the crucible and is supported in a clearance hole through the insulating plug. The wires are taken through brass tubes screwed into the sealing plate and sealed off by short lengths of clipped rubber tubing. There is a gas inlet (W) screwed into the seal.

The balance (X) is supported on the slate shelf above the furnace and thus protected from radiation. (There was no measurable alteration in zero during an experiment such as might be caused by unequal heating of the beam.) The balance is of the assay type converted to the "Chainomatic" principle and the pointer is replaced by an aluminium strip which carries a graduated scale. A lamp, projection lens and ground glass screen enable readings of the zero position to be made much more quickly and accurately than with the conventional pointer. Such provision is necessary in this work since very small movements of the pointer mean considerable differences in the values of surface tension obtained when the maximum pull is reached. These alterations to the original balance,

especially the "semi-continuous" weighing make the measurement of the maximum pull, while the furnace is being lowered, a much simpler operation.

The dipping cylinder (Y) is of platinum, 10% rhodium alloy and is formed from a straight-sided, thimble crucible $\frac{3}{4}$ ins. deep and $\frac{1}{2}$ ins. diameter. Air holes are drilled in the bottom and the cylinder is suspended by a thin platinum tube riveted to the bottom end. This arrangement was found to be very much more satisfactory than the conventional wire stirrup. Levelling of the cylinder was more easily carried out and no tilting was experienced during an experiment. The cylinder is suspended from the balance by links of aluminium wire outside the furnace and a chain made from fine platinum wire inside the furnace. The linkage ensures that the cylinder hangs vertically.

Measurement of the cylinder diameter is important since this gradually changes in service, probably due to differential contraction between the cylinder and the film of solid slag which remains after an experiment. The best method was found to be to mount the cylinder horizontally on a small table so that it could be rotated on its own axis and measure the diameter by a travelling microscope,

accurate to 0.0005cm. Illumination of the edge required to be standardised to obtain good results. Measurements were taken across ten, evenly-spaced diameters.

It is important, as Harkins and Jordan[18] have shown, that the cylinder should have its edge in a horizontal plane. Levelling is accomplished by a small, polished brass table mounted on three screwed legs. The cylinder is suspended over this, almost touching and observed against a white background, the table having first been levelled by an accurate spirit-level. It is easy to detect very small angles of tilt and to correct this by bending the suspension tube slightly.

Accuracy of Results.

In its present form the apparatus is capable of measuring surface tension with considerable accuracy. It is very difficult to assess the probable error of the results on slags. Measurement of the cylinder perimeter can be carried out to 0.04% while the balance is capable of weighing to 0.002%. The maximum error in the result if no others are takeninto account is then 0.05%. Contributory errors are those due to tilting of the cylinder, maximum probably 0.2% and the surface of liquid not being quite plane, not more than 0.05%. From all these sources the error is not likely to rise above 0.3%. If the contact angle between cylinder and liquid is not zero the error may rise to about 0.8%, (excluding abnormal cases of large contact angles). Non-uniform wetting of the cylinder may introduce an error of slightly lesser magnitude.

During measurements on slags convection currents etc., reduce the possible accuracy of weighing to about 0.02%. The viscosity of the slag is also likely to affect the conditions of attachment of the slag to the cylinder. It seems safe to say that the probable accuracy of isolated results is about 1.0%. In a series of readings on one slag conducted under similar conditions, the error must be less

than this, to judge by the reproducibility of the results. It is probably not true to say this of the more viscous slags where a certain amount of judgement is necessary in assessing the value of the results. An additional error is, of course, present in the temperature measurement. A Cambridge potentiometer measures the E.M.F. generated by the thermocouple to $\pm$ 0.005 Mv. The thermocouple is supplied from a batch standardised by the N.P.L. but additional standardisation was carried out using the gold and palladium wire method. This was found to agree very closely with the standardisation supplied. The couple was checked at intervals which showed that the E.M.F. fell by about 0.1 mv. over the period of the research. This is probably due to preferential volatilisation of rhodium. Cold junction temperatures were measured and the appropriate correction applied.

Experiments in which the platinum crucible was filled with a low melting glass, fairly viscous, and another thermocouple was inserted in the glass showed that there was a difference of only 1 or 2 degrees between the temperature of the glass and the temperature recorded by the permanent thermocouple provided the furnace was not heating or cooling rapidly. The thermocouple was sheathed

in the experiments on iron silicate to prevent accidental contact with the iron crucible. A correction has not been applied for the temperature drop across the sheath since it was of very thin mullite tubing.

Materials.

SiO_2 - pure crystalline quartz, heated to 900°C., quenched in water and crushed in a hammer mill and an agate mortar to about 200-300 mesh. Iron, mica etc., removed by prolonged extraction with hot, hydrochloric acid. Purity 99.8%.

MnO - from pure manganous oxalate by heating in a nitrogen-hydrogen atmosphere to 1000°C. in a Kanthal-wound furnace (mullite tube). Purity varies with different samples but between 97.5 and 98.5% MnO.

CaO - by ignition of A.R. calcium carbonate - weighed as carbonate, then ignited before use.

MgO - pure crystalline magnesia - ground to about 150 mesh. Purity about 99%.

Al_2O_3 - pure anhydrous alumina (Hopkin and Williams).

FeO - from pure ferrous oxalate by heating in vacuo in a Kanthal-wound furnace with iron tube up to 1000°C. Heating is not continuous - pauses are made for drying out at 200°C. and for removal of water and CO_2 at 700°C. - product quenched from 1000°C. still under vacuum. A completely vacuum-tight system is essential to ensure that the product contains no Fe_3O_4. The product is black

and practically of the pure wüstite composition if prepared carefully.

Preparation of Slags.

The crucible in use is too shallow to permit direct melting of the slags from the powdered materials a sufficient weight of which occupies too great a volume. Slags were therefore prepared separately. All slags except those containing MnO or FeO were prepared by weighing out the required quantities, mixing by alternate grinding together and shaking in a stoppered bottle and melting in a carbon crucible with a Philips' high-frequency induction heater. Carbon is the only suitable container since it is a conductor, and both refractory and resistant to slag attack. The crucible is covered and a nitrogen atmosphere is maintained inside to prevent ash formation which might contaminate the slag. The slags were allowed to remain molten for a short time only, then cooled and ground in an agate mortar. They were ignited in oxygen for several hours as some reduction by carbon cannot be prevented, e.g. with lime silicates some calcium carbide is formed.

Iron and manganese silicates were melted in an Armco iron crucible in a platinum-wound tube furnace.

An atmosphere of purified nitrogen was used for the iron slags and cracked ammonia for the manganese slags. The iron slags lose some oxygen with the result that the wüstite approaches the Fe_0 composition. Manganese slags pick up a little iron (up to 1% - see Towers and Gworek[33]) but in both cases alteration in composition is minimised by rapid melting and cooling.

Each slag was rendered homogeneous by soaking above the melting point after transference to the platinum basin used in actual measurements. An exception to this is the iron silicate, which, in contact with an iron crucible, picks up iron as the experiment continues. Pick up is much more rapid at high temperatures and seems to be very small indeed when the slag is being cooled. According to Kozakevitch[4] pick up of iron is only serious when the temperature is raised.

Method of Measurement.

The procedure outlined below has been followed with all the slags used. After the initial soaking the slag was allowed to cool slowly until solid; this may be important. (See p. 57). The temperature was then raised to about 50°C. above the melting point of the slag; generally the viscosity was rather high at lower temperatures to allow of accurate readings. The weight of the clean cylinder was determined (its diameter having been measured previously) and the balance beam rest set so that the beam could oscillate one scale division on either side of the zero. The weight was increased slightly to keep the beam down against the stop and the furnace was then raised until the cylinder made contact with the slag. This point was indicated by the sudden swing of the scale to the opposite side of the zero. Weights were then added, the furnace being lowered meanwhile, until the maximum was reached, the beam being constrained by the rest to swing only one division on either side of the zero. Near the maximum additional weight was added very slowly by the chain, the furnace being lowered meanwhile, with intervals long enough to allow viscous slags to come to an equilibrium position.

The additional weight was adjusted so as to keep the scale

always at the zero position. This is quite easily done since oscillation of the beam is very slow and restricted in range of movement with all but the very fluid slags. The maximum is indicated by the point at which further addition of weight causes a sudden swing of the scale to the left and further lowering of the furnace will not bring it back to zero. If this swing is restricted by the beam rest the liquid column raised by the cylinder does not break and the scale may be brought back to zero by removing about thirty milligrams. The procedure may then be repeated, after raising the furnace a little, to fix the maximum more accurately. A temperature reading is taken immediately the pull has been measured.

Calculation of the surface tension is carried out as follows. From the values of the maximum pull (m) and the cylinder diameter (D) the apparent surface tension p is calculated from the formula:-

$$p = \frac{m}{2\pi D}$$

The cylinder diameter must be corrected for expansion at higher temperatures. A value of 8.8×10^{-6} has been selected for the linear coefficient of expansion of the platinum, rhodium alloy.

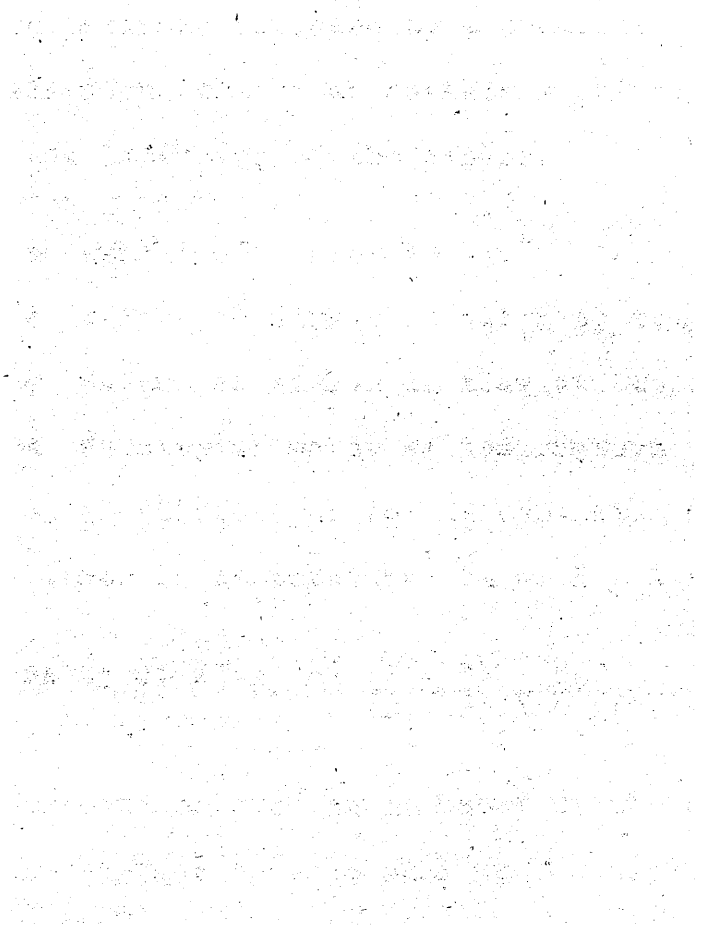
From the cylinder radius R and the liquid density d the value of $\frac{R^3}{V}$ is calculated. The graph of $\frac{R^3}{V}$ and $\frac{\gamma}{\rho}$ gives the correction factor $\frac{\gamma}{\rho}$. The value of γ is then given by multiplying ρ by the correction factor.

In initial experiments the liquid column was not allowed to break during a run. Readings were taken at one temperature and, while the slag was heating or cooling to the next temperature, the furnace was kept slightly raised, so that the required balancing weight was about 0.1 gm. short of maximum. This method is certainly easier than immersing the cylinder every time a measurement is desired but may give rise to inaccuracy. With the more viscous slags wetting of the cylinder is not always perfectly reproducible so that, at the same temperature, slightly different values for surface tension may be obtained with repeated immersions. Accordingly, the procedure has been to break the liquid column after every measurement and re-immerse the cylinder for the next. At each temperature two readings are taken to check that the cylinder is properly wetted. Babcock[5] reports that such a procedure is necessary for molten glasses which are generally much more viscous.

The viscosity of the slag has a considerable influence on the measurement of surface tension. With very fluid slags such as $2MnO.SiO_2$, the measurement is as simple as with water. Viscous slags, e.g. calcium aluminium silicates, cannot be measured with the same accuracy. This is due, in part, to the reduction in sensitivity caused by sluggish movement of the balance. (For this reason the sensitivity of the balance is adjusted to limits which would not be suitable for normal weighing).

An additional factor is that with viscous slags, the equilibrium shape of liquid surface for any position of the cylinder above the slag surface is reached very slowly. It was noticed that when the maximum pull is first measured a considerable weight has to be removed before the balance beam will return to its zero position. Repeat measurements, without breaking the liquid column, give smaller values for the maximum pull. A steady value is soon reached, lower than the first by about 0.05-0.1 gm., at which the slag behaves just as other liquids; this is the correct value and is reproducible. Babcock[5] notes that it is possible to obtain values too low by stretching the column beyond the maximum point. High viscosity permits this condition to obtain for some time, whereas,

with fluid liquids the column simply breaks beyond the maximum.



Measurement of Slag Density.

To apply the corrections of Harkins and Jordan to the surface tension results the density of the liquid slags must be known. No record is available so some densities have been measured by the method of Archimedes. The same apparatus as for surface tension is used except that the platinum cylinder is replaced by a platinum sinker. The shallow basin is replaced by a crucible $1.\frac{1}{4}$ ins. diameter and $1.\frac{1}{2}$ ins. deep, which can contain a sufficient depth of slag to allow immersion of the sinker.

If B = weight of sinker in air

W = weight of sinker in water at temperature t_0

S = weight of sinker in slag at temperature t_1

d_0 = density of water at temperature t_0

λ = coefficient of volume expansion of sinker.

Volume of sinker at temperature $t_1 = \frac{B - W\,(1 + \lambda(t_1 - t_0))}{d_0}$

$$\text{True density of slag} = \frac{(B - S)\ d_0}{(B - W)(1 + \lambda(t_1 - t_0))}$$

Corrections for the upthrust on the suspension wire and the surface tension pull on the wire where it enters the liquid have not been made, since the wire is so fine that these do not influence the final result appreciably.

Slag Composition (by wt.)	Liquid Density gms./cc.	
	Measured	Calculated
70.0% MnO 30.0% SiO_2	3.42	-
62.0% MnO 38.0% SiO_2	3.27	-
54.2% MnO 45.8% SiO_2	3.12	-
52.0% MnO 48.0% SiO_2	-	3.10
48.3% CaO 51.7% SiO_2	-	2.40
44.0% CaO 56.0% SiO_2	-	2.39
40.0% CaO 60.0% SiO_2	-	2.38
38.0% MgO 62.0% SiO_2	-	2.39
75.0% FeO 25.0% SiO_2	--	3.84
Rhodonite + 5% Al_2O_3	-	3.18
Rhodonite + 10% Al_2O_3	-	3.24
CaO/SiO_2 = 1.2 + 17.65% Al_2O_3	-	2.51
CaO/SiO_2 = 1.2 + 26.87% Al_2O_3	-	2.60
$CaO.SiO_2$ + 10% MgO	-	2.40
$CaO.MgO.2SiO_2$	-	2.40
20.3% MgO 61.4% SiO_2 18.3% Al_2O_3	-	2.39
27.65% MgO 55.56% SiO_2 16.64% Al_2O_3	-	2.41
50.0% CaO 50.0% Al_2O_3	-	2.64

Table 2.

Liquid densities of Slags.

(at 100°C. above melting point.)

Measurements of density have been made on three manganese silicates, rhodonite, tephroite and the eutectic composition. The solid densities have also been measured by the specific gravity bottle method.

The measurement of liquid density is a considerable complication to the measurement of surface tension. It has been found that an accurate figure is not necessary, e.g. a variation in the figure for tephroite of 5% affects the correction factor only to the extent of 0.5%, i.e. approximately 2.5 dynes/cm. in the surface tension value of 502 dynes/cm. Other errors can be as large as this, as the preceding section has shown. Accordingly, only the solid densities of all other slags have been measured. The liquid density is taken as 85 to 90% of this figure depending on the stability of the compound as indicated by the surface tension results. (See p.87). It is considered that these figures have rather better than the 5% accuracy indicated above.

The measured and calculated densities are grouped in Table 2 .

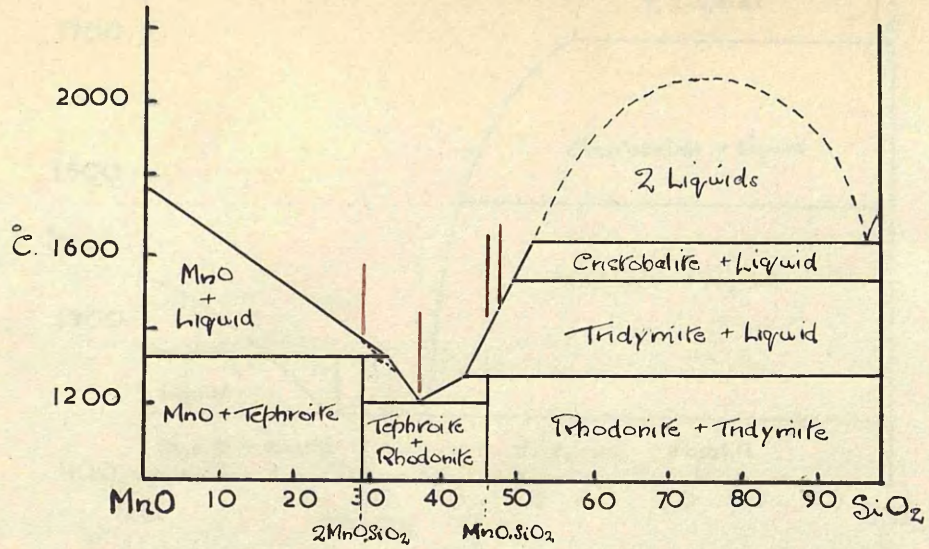
Part V.

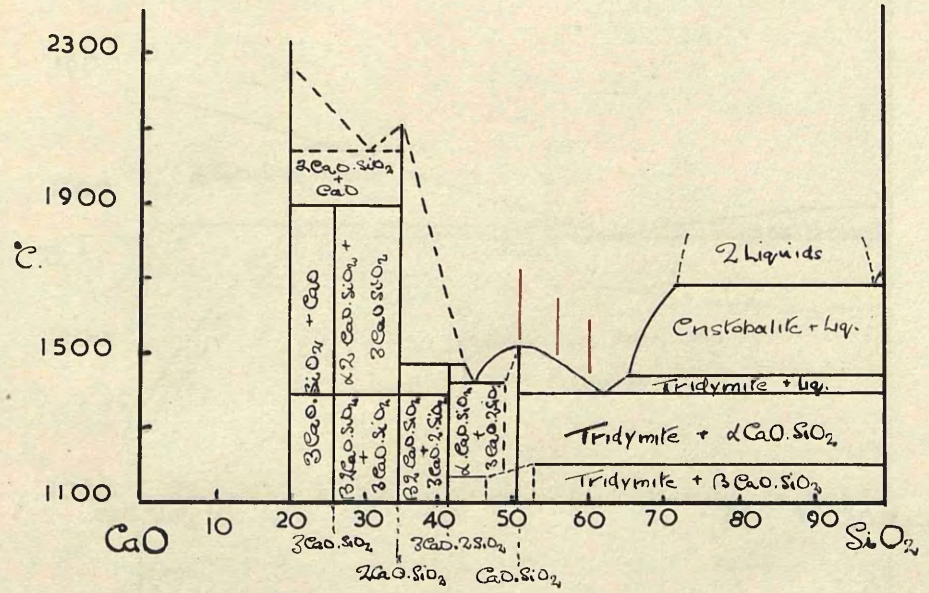
Results.

Experimental Work and Results.

The pattern of the experimental work has followed a speculative rather than a carefully planned trend. A manganese silicate of the rhodonite composition was the first slag investigated because of previous work conducted upon it[18]. The discovery that the surface tension of this slag increased with temperature, a behaviour shown only by molecularly-associated liquids, influenced the choice of slags for further investigation. Interest centred on the temperature coefficient of surface tension rather than the actual value of the surface tension.

The number of compositions available for investigation is limited by the maximum temperature at which the platinum furnace can be used. It was not considered wise to take readings above 1610°C. though some measurements are recorded up to 1617°C. Most workers with platinum-rhodium furnaces recommend their use at temperatures below 1550°C[34]. The winding of the furnace has since been inspected and shows little evidence of serious volatilisation of platinum. This does not mean that all slags with melting temperatures below 1610°C. can be used. Readings must be started sufficiently far above the melting point of the slag for it to be reasonably fluid, otherwise the possible error of the results is


2000
°C. 1600
1200
MnO + Liquid
MnO + Tephroite
Tephroite + Rhodonite
2 Liquids
Cristobalite + Liquid
Tridymite + Liquid
Rhodonite + Tridymite
MnO
10 20 30 40 50 60 70 80 90
SiO2
2MnO.SiO2
MnO.SiO2


2300
1900
°C.
1500
1100
3CaO.SiO2 + CaO
3CaO.SiO2
2 Liquids
Cristobalite + Liq.
Tridymite + Liq.
Tridymite + αCaO.SiO2
Tridymite + βCaO.SiO3
CaO
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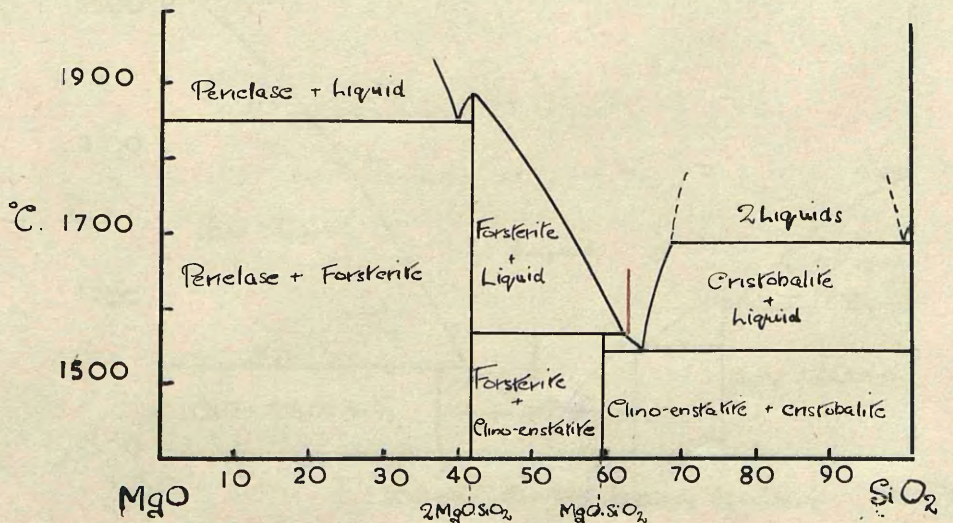
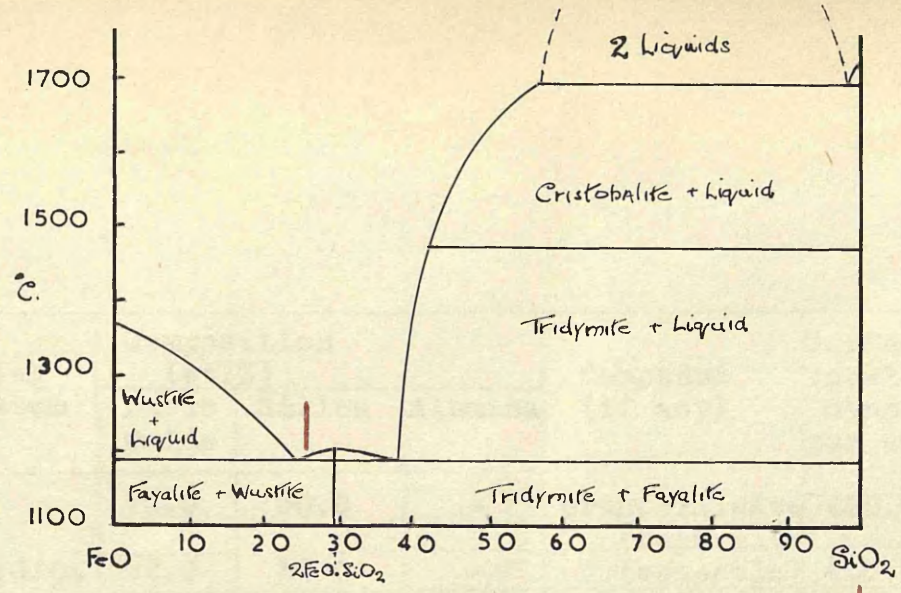
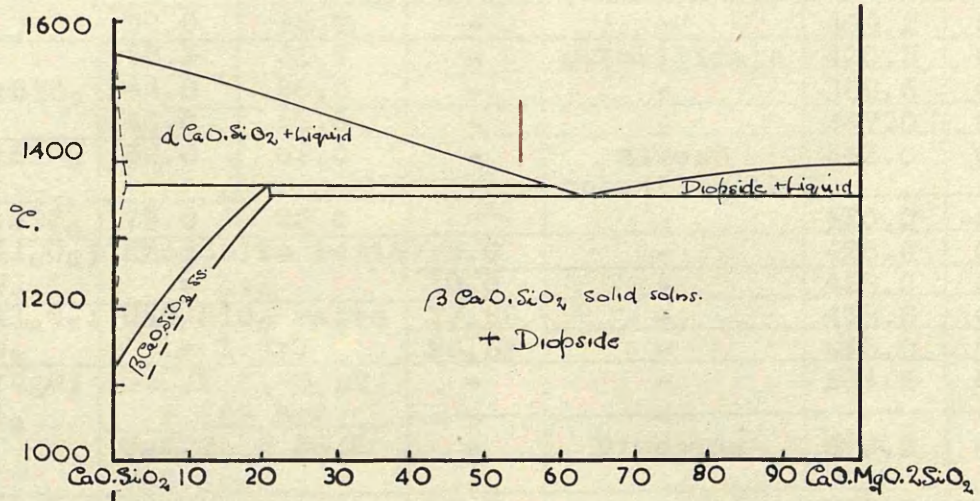
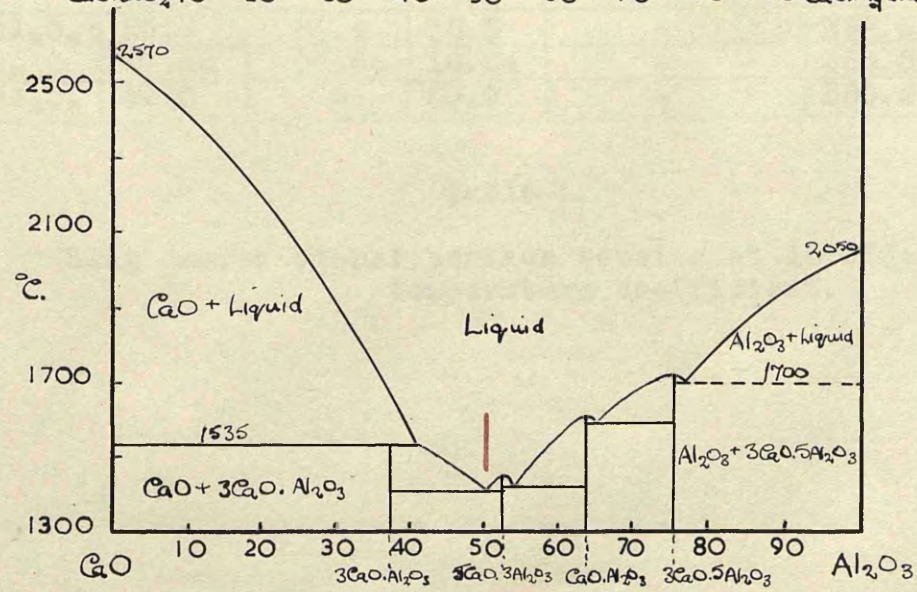
SiO2
3CaO.SiO2
2CaO.SiO2
3CaO.2SiO2
CaO.SiO2


1900
°C. 1700
1500
Periclase + liquid
Periclase + Forsterite
Forsterite + Liquid
2 Liquids
Cristobalite + liquid
Forsterite + Clino-enstatite
Clino-enstatite + cristobalite
MgO
10 20 30 40 50 60 70 80 90
SiO2
2MgO.SiO2
MgO.SiO2


2 Liquids
Cristobalite + Liquid
Tridymite + Liquid
Wustite + Liquid
Fayalite + Wustite
Tridymite + Fayalite
1700
1500
1300
1100
°C.
FeO
10 20 30 40 50 60 70 80 90
SiO2
2FeO.SiO2


α CaO.SiO2 + Liquid
Diopside + Liquid
β CaO.SiO2 solid solns.
+ Diopside
βCaO.SiO2 ss
1600
1400
1200
1000
°C.
CaO.SiO2
10 20 30 40 50 60 70 80 90
CaO.MgO.2SiO2


2570
2050
CaO + Liquid
Liquid
Al2O3 + Liquid
1700
1535
CaO + 3CaO.Al2O3
Al2O3 + 3CaO.5Al2O3
2500
2100
1700
1300
°C.
CaO
10 20 30 40 50 60 70 80 90
Al2O3
3CaO.Al2O3
3CaO.3Al2O3
CaO.Al2O3
3CaO.5Al2O3

Slag system	Composition (wt.%)			Compound (if any)	Surface tension dynes per cm.	Temp. coeff. dynes/cm./°C.
	Basic Oxide	Silica	Alumina			
$MnO;SiO_2$	70.0	30.0	-	orthosilicate (tephroite)	492.0	0.015
	62.0	38.0	-	(eutectic)	460.2	0.047
	54.2	45.8	-	metasilicate (rhodonite)	415.1	0.086
	52.0	48.0	-	-	409.2	0.086
$CaO;SiO_2$	48.3	51.7	-	metasilicate	400.5	0.021
	44.0	56.0	-	-	389.5	0.033
	40.0	60.0	-	-	367.0	0.040
$MgO;SiO_2$	38.0	62.0	-	almost metasilicate	363.0	0.098
$FeO;SiO_2$	75.0	25.0	-	-	450.0	-0.006
$MnO;Al_2O_3;SiO_2$	Rhodonite ratio = 1:1		5.0	-	426.0	0.063
			10.0	-	428.0	0.061
$CaO;Al_2O_3;SiO_2$	CaO/SiO_2 ratio = 1.2:1		17.65	-	438.8	0.018
			26.87	-	446.0	0.010
$CaO;MgO;SiO_2$	CaO/SiO_2=0.67 + 10% MgO		-	-	384.5	0.029
			-	-		
	CaO.25.9 55.5 MgO.18.6		-	Diopside	376.5	0.048
$MgO;Al_2O_3;SiO_2$	20.3	61.4	18.3	-	329.0	0.025
	27.65	55.56	16.64	-	356.8	0.058
$CaO;Al_2O_3$	50.0	-	50.0	-	580.2	-0.046

Table 3.

Slag compositions: surface tension at 1570°C: mean temperature coefficient.

54.2% MnO 45.8% SiO_2

	Heating				Cooling	
	Temp. °C.	S.T. dynes/cm.	Temp. °C.	S.T. dynes/cm.	Temp. °C.	S.T. dynes/cm.
	1465	403.1	1540	408.3	1587	413.7
	1470	402.2	1546	409.0	1585	413.9
	1478	402.8	1550	409.6	1577	413.7
1st	1485	403.2	1569	411.2	1564	413.1
Run	1491	404.0	1573	411.5	1558	412.9
	1508	405.6	1580	412.1	1549	412.8
	1519	406.5	1587	412.7	1528	412.5
	1528	407.1	1592	413.0	1515	411.9
	1533	407.8	1598	413.9	1500	411.7
		Heating			Cooling	
	1453	406.0	1529	412.3	1558	414.5
2nd	1456	406.3	1566	413.7	1546	414.4
Run	1486	409.0	1572	415.3	1536	413.3
	1491	409.4	1574	415.4	1474	409.8
		Heating			Cooling	
	1461	407.2	1501	410.8	1527	413.0
	1470	407.6	1510	411.3	1509	412.5
3rd	1476	408.1	1513	411.8	1488	411.5
Run	1479	408.1	1524	412.3	1476	411.0
	1482	408.3	1535	413.2		
	1485	407.9	1541	413.2		
	1496	410.0	1542	413.1		

Table 4.

Surface tension of rhodonite at different temperatures.

70.0% MnO 30.0% SiO_2

Heating				Cooling	
Temp. °C.	S.T. dynes/cm.	Temp. °C.	S.T. dynes/cm.	Temp. °C.	S.T. dynes/cm.
1401	490.0	1520	491.6	1575	492.7
1425	490.3	1537	491.7	1505	492.7
1431	490.4	1544	491.9	1532	492.8
1437	490.5	1544	491.9	1486	492.7
1451	490.5	1565	492.0	1451	492.4
1462	490.6	1576	492.2	1445	492.3
1469	490.8	1581	492.4	1440	492.3
1479	490.9	1586	492.4	1382	491.8
1487	490.9	1591	492.5		
1492	491.0	1596	492.6		
1505	491.4	1600	492.6		

62.0% MnO 38.0% SiO_2

Heating				Cooling	
1316	448.1	1544	459.8	1576	460.5
1321	448.8	1548	459.9	1514	459.9
1327	449.0	1565	460.0	1455	458.7
1386	452.3	1578	460.3	1415	457.3
1425	454.0	1588	460.6	1407	456.4
1462	456.3	1597	460.9		
1504	458.1	1599	461.0		

52.0% MnO 48.0% SiO_2

Heating				Cooling	
1488	404.2	1575	409.4	1575	410.4
1514	405.8	1606	413.2	1556	409.5
1543	404.5	1607	413.9	1545	407.5
				1460	405.9

Table 5.

Surface tension of tephroite and other manganese silicates at different temperatures.

48.3% CaO 51.7% SiO_2

Heating				Cooling	
Temp. °C.	S.T. dynes/cm.	Temp. °C.	S.T. dynes/cm.	Temp. °C.	S.T. dynes/cm.
1570	401.8	1598	401.3	1596	401.0
1584	401.4	1609	401.3	1586	399.9
1589	401.4	1610	401.3	1564	399.7
1595	401.4	1616	401.3	1539	399.1

44% CaO 56% SiO_2

Heating				Cooling	
1560	388.6	1580	390.2	1554	389.5
1568	389.0	1592	390.3	1527	389.3
1574	389.1	1607	390.6		
1578	389.8				

40% CaO 60% SiO_2

Heating				Cooling	
1522	365.3	1565	367.1	1568	367.1
1521	365.3	1577	367.6	1543	367.3
1539	365.9	1589	367.9	1519	367.0
1551	366.6	1602	368.3		

38% MgO 62% SiO_2

Heating			
1567	363.6	1600	367.0
1580	365.0	1607	368.0
1591	364.9	1617	368.6

75% FeO 25% SiO_2

Cooling				Cooling	
1465	450.8	1368	451.1	1289	450.7
1439	451.0	1340	451.6	1261	450.6
1399	451.0	1329	451.6	1243	450.3

Table6.

Surface tension of calcium silicates, magnesium silicate and iron silicate at different temperatures.

Rhodonite + 10% Al_2O_3

Heating				Cooling	
Temp. °C.	S.T. dynes/cm.	Temp. °C.	S.T. dynes/cm.	Temp. °C.	S.T. dynes/cm.
1336	412.3	1490	423.5	1500	427.1
1362	416.2	1497	423.9	1431	423.9
1381	417.0	1520	425.3	1381	420.6
1404	418.5	1546	426.8	1336	417.7
1423	419.5	1566	428.8		
1441	421.0	1571	428.8		
1455	422.0				

Rhodonite + 5% Al_2O_3

Heating				Cooling	
1375	414.0	1479	420.8	1520	424.2
1378	415.1	1511	422.9	1417	419.1
1382	415.5	1541	424.4	1324	414.0
1412	417.1	1574	426.1	1316	413.9
1445	419.2	1578	426.3		

CaO/SiO_2 = 1.2 + 17.65% Al_2O_3

Heating			
1498	436.9	1568	438.4
1503	437.5	1576	438.6
1521	437.8	1589	439.0
1541	438.1	1592	440.1

CaO/SiO_2 = 1.2 + 26.87% Al_2O_3

Heating				Heating	
1428	444.9	1505	446.0	1573	446.1
1430	445.0	1506	445.0	1575	446.2
1426	444.9	1507	445.6		
1466	445.4	1548	445.8		

Table 7.

Surface tension of manganese and calcium alumino-silicates at different temperatures.

50% CaO 50% Al_2O_3

Heating				Heating	
Temp. °C.	S.T. dynes/cm.	Temp. °C.	S.T. dynes/cm.	Temp. °C.	S.T. dynes/cm.
1420	586.3	1519	582.8	1603	578.0
1460	585.1	1540	580.2		
1493	584.4	1580	579.4		

CaO-SiO_2 + 10% MgO.

Heating					
1501	382.9	1544	383.9		
1515	383.0	1561	384.0		
1536	383.7	1574	384.6		
1540	383.8	1600	385.0		

CaO.MgO.2SiO_2 (diposide)

Heating				Cooling	
1447	370.5	1502	373.2	1501	375.5
1452	372.2	1533	375.8	1438	373.2
1458	372.2	1558	376.5		
1460	372.0	1584	377.0		
1481	372.9	1601	378.2		

20.3% MgO 61.4% SiO_2 18.3% Al_2O_3

Heating				Cooling	
1539	328.1	1588	329.0	1590	329.9
1544	328.6	1596	329.4	1589	329.5
1562	329.8			1587	329.8
1580	329.9			1504	328.2
1582	328.9			1506	328.4

27.61% MgO 55.6% SiO_2 16.64% Al_2O_3

Heating				Cooling	
1537	354.1	1589	358.6	1537	356.4
1538	354.5	1608	359.9	1492	353.7
1566	356.4				

Table 8.

Surface tension of calcium aluminate, calcium magnesium silicates and magnesium aluminium silicates at different temperatures.

larger than the change in surface tension over a reasonable temperature interval. A temperature range of at least 100°C. above this fluid temperature must also be available, since the temperature coefficient may be as small as 0.015 dynes/cm./°C. i.e. 1.5 dynes in 100°C. The reproducibility of results is only slightly better than this even for fluid slags. It is impossible, therefore, to investigate slags which have high percentage of silica or basic oxide; in either case the melting points are high.

The compositions of the slags are listed in Table 3, which also includes the value of the surface tension at 1570°C. (the value for iron silicate being obtained by extrapolation) and the mean temperature coefficient over the range investigated. Tables 4. to 8. show the individual results for each slag, for purposes of reference. The appropriate equilibrium diagrams are also given to facilitate interpretation of the results.

All the surface tension values are high, ranging from 580 dynes/cm. for the calcium aluminate slag to 329 dynes/cm. for a magnesium, aluminium silicate. In comparison with glasses[35] the values are of the order expected for slags which contain much higher percentages

of basic oxide. The value for the iron silicate agrees well with that of Kozakevitch[4].

The most striking feature of the results is that all the slags except the iron silicate and calcium aluminate show positive temperature coefficients of surface tension. These are very small in the case of calcium metasilicate, manganese orthosilicate and the lime, alumina silicates but are large for manganese and magnesium metasilicates. The various compositions have been chosen to show the effect on the surface tension and temperature coefficient of:-

1. variation in silica contact within binary systems
2. variation from one binary system to another.

Subsidiary effects are shown by additions of alumina to binary slags.

The effect of the first factor is illustrated by the manganese and calcium silicate slags (see Table 3.). In the $MnO-SiO_2$ system the value of the surface tension falls from 492.0 dynes/cm. at 30% silica to 409.2 dynes/cm. at 48% silica, while the temperature coefficient increases from 0.015 dynes/cm/°C. to 0.086 dynes/cm./°C. In the $CaO-SiO_2$ system surface tension falls from 400.5 dynes/cm. at 51.73% silica to 367.0 dynes/cm at 60% silica while

the temperature coefficient increases from 0.021 dynes/cm./°C. to 0.04 dynes/cm./°C.

The effect of the second factor can only be illustrated by comparison between compositions containing the same molar percentage of silica. If the metasilicate composition be taken in each case the surface tension varies as follows. (Note: the magnesium silicate used contains 3% more silica than the metasilicate which has too high a melting point. The surface tension of the $MgO.SiO_2$ composition is probably 10 dynes/cm. higher than that quoted here, to judge from the effect of silica on the other oxides.)

$MnO.SiO_2$	415.1 dynes/cm.
$CaO.SiO_2$	400.5 dynes/cm.
$MgO.SiO_2$	363.0 dynes/cm.

The results of Kozakevitch[4] can be extrapolated to give a value of 365 dynes/cm. for iron metasilicate.

This order is not paralleled by the temperature coefficient which falls in the order Mg, Mn, Ca for these three metasilicates. The positive temperature coefficient therefore becomes smaller as the size of the cation present in the slag decreases.

The effect of alumina has been shown by adding 5%

and 10% Al_2O_3 to slags containing the rhodonite ratio of MnO to SiO_2 (1.0) and 17.5% and 27% Al_2O_3 to slags of CaO to SiO_2 ratio equal to 1.2. Alumina has also been added to two magnesium silicates. In all cases alumina raises the surface tension, the first addition being the more effective. Thus, the surface tension of rhodonite is raised by 11 dynes/cm. with the addition of 5% Al_2O_3 and only by a further 2 dynes/cm. with the addition of a further 5% Al_2O_3. Alumina also seems to reduce the positive temperature coefficient slightly. The addition of 10% alumina to rhodonite reduces the temperature coefficient from0.086 dynes/cm./°C. to0.061 dynes/cm./°C. The effect is more difficult to observe with the calcium aluminium silicates since the temperature coefficient is small to begin with, though these slags also show the effect of alumina in raising the surface tension.

The surface tension and temperature coefficient vary across the pseudo-binary system $CaO.SiO_2$ - $MgO.SiO_2$ in a regular fashion. Diopside ($CaO.MgO.2SiO_2$) shows a surface tension of 376.5 dynes/cm. which is practically a mean between that of $CaO.SiO_2$ (400.5 dynes/cm.) and $MgO.SiO_2$ (363 dynes/cm.) while the temperature coefficients are in a similar relationship.

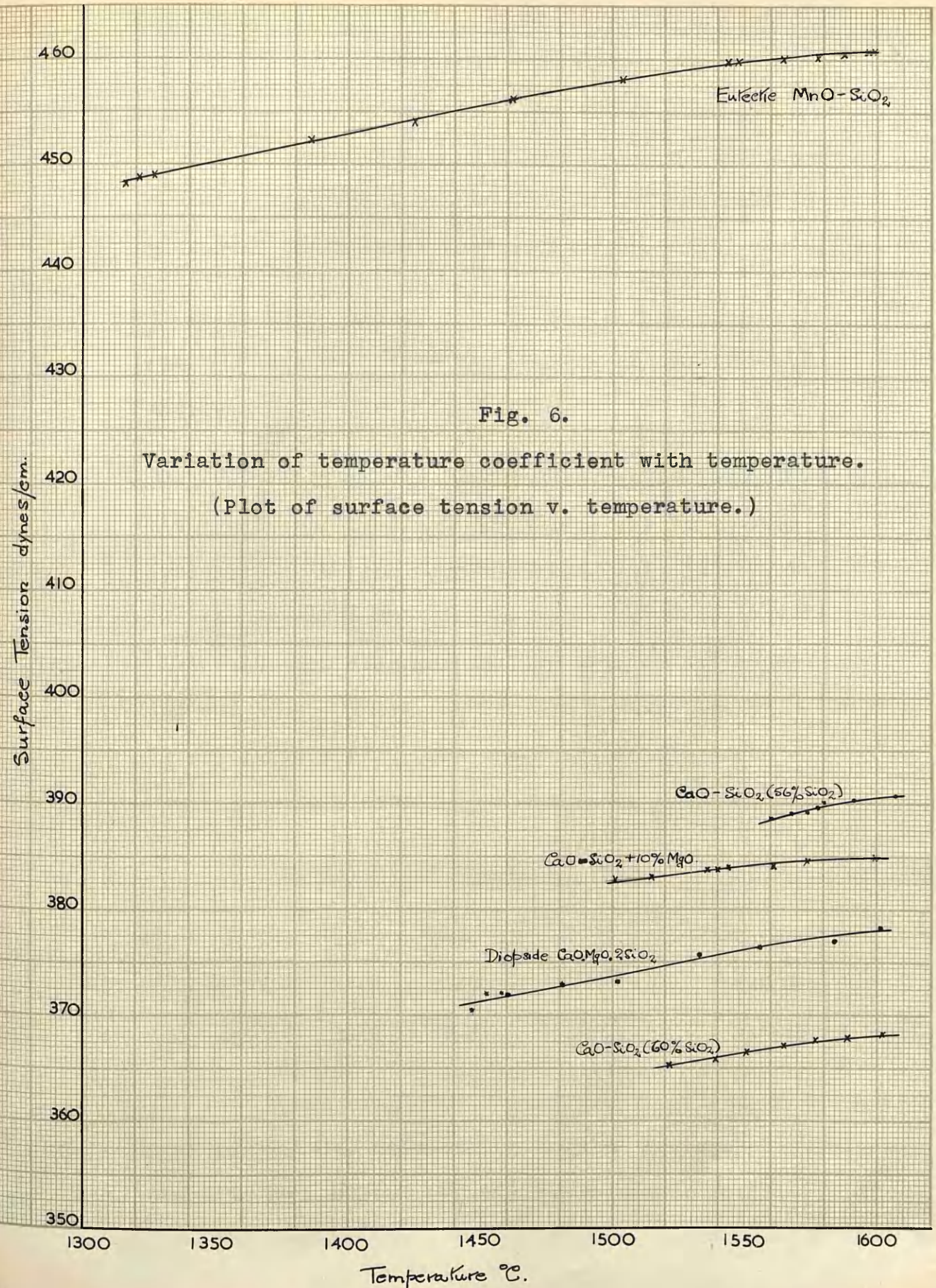


Fig. 6.

Variation of temperature coefficient with temperature.

(Plot of surface tension v. temperature.)

The calcium aluminate slag shows the only markedly negative temperature coefficient; it also possesses the highest surface tension of all the slags investigated.

These points are further discussed in Parts VII and VIII but two other features of the results are noticeable.

Firstly, the temperature coefficient of surface tension is not constant for some slags but decreases gradually at higher temperatures. This is obvious only for the eutectic $MnO-SiO_2$ composition, diopside, $CaO-SiO_2$ + 10% MgO slag and the two calcium silicates, 56% and 60% SiO_2. These results are plotted in Fig. 6 on a fairly large scale. For the eutectic manganese silicate the temperature coefficient varies as follows.

Temperature range °C.	Mean temperature coefficient dynes/cm./°C.
1300 - 1400	+ 0.055
1400 - 1500	+ 0.052
1500 - 1600	+ 0.033

These slags are distinguished by one of two features viz. low melting point which enables a large temperature range to be covered, or small temperature coefficient.

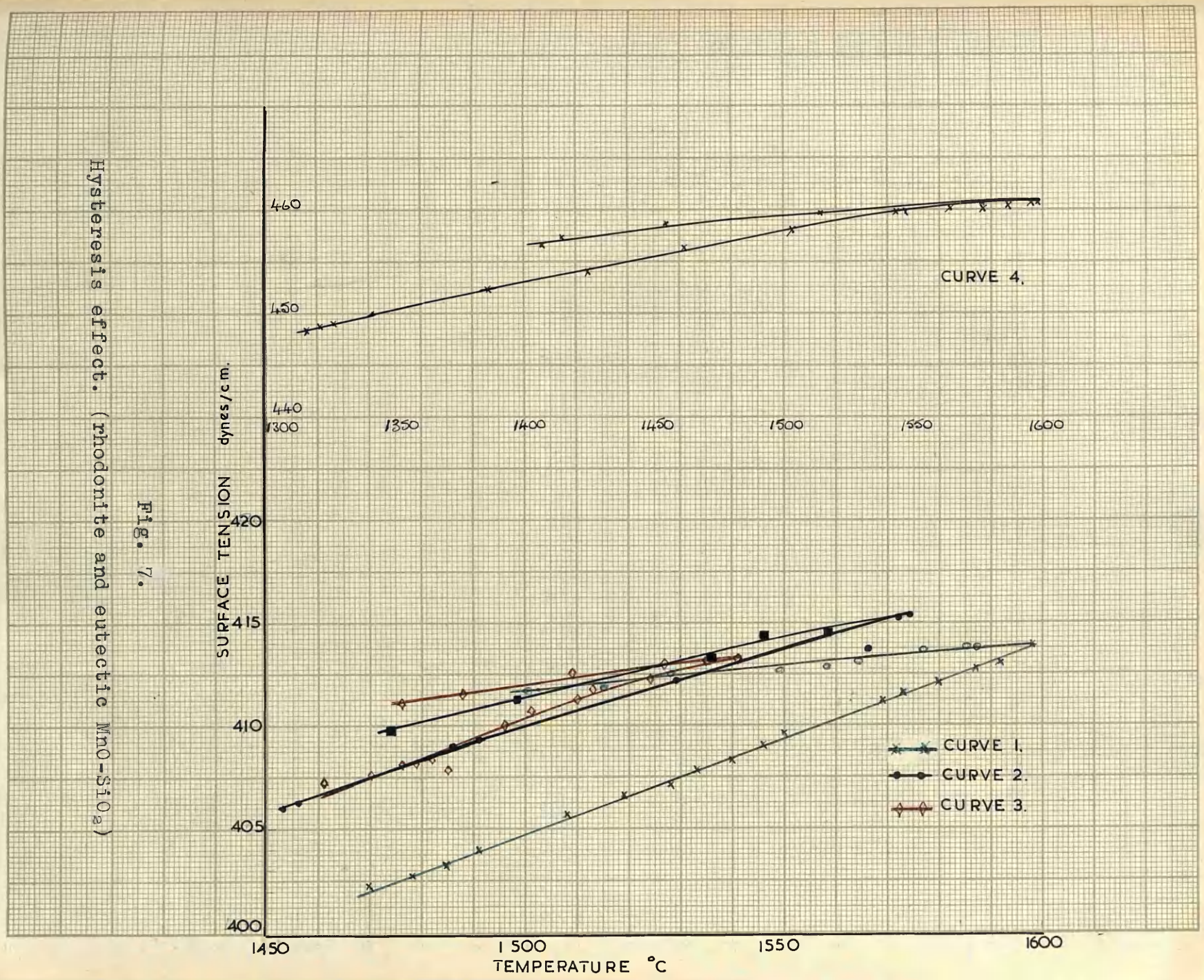


Fig. 7.

Hysteresis effect. (rhodonite and eutectic MnO-SiO2)

Secondly, the surface tension results reveal an hysteresis effect on heating and cooling. Three sets of results for a slag of rhodonite composition, plotted in Fig. 7 illustrate this effect quite clearly. Normally, measurements of surface tension were made on heating, sufficient time being allowed for stabilising the temperature while a reading was being taken. The readings taken on cooling were always slightly higher, the divergence being greater at low temperatures. Allowing the slag to stand at any one temperature for a considerable time, up to 45 minutes, lowered the reading slightly, but it was not possible to reach exactly the value obtained on heating, though the difference could be as small as 0.5 dyne/cm. Rapid cooling from high temperatures until the slag was solid and subsequent remelting gave values higher than those originally obtained on heating. Thus, curve (1) in Fig. 7 is obtained on the first melting (after slow cooling from the soaking temperature). Curve (2) is taken on remelting after rapid cooling from 1600°C. Curve (3) is obtained on remelting after an intermediate rate of cooling from 1600°C. The value of the surface tension can therefore be influenced by the previous history of the slag. The eutectic slag, curve (4), also shows this marked hysteresis.

Castor Oil

Heating				Cooling	
Temp. °C.	S.T. dynes/cm.	Temp. °C.	S.T. dynes/cm.	Temp. °C.	S.T. dynes/cm.
22.0	35.5	30.0	34.8	55.5	33.5
24.5	35.4	55.0	33.6	27.5	35.5
26.5	35.2	56.0	33.55		

Sodium Chloride

Heating				Cooling	
810	111.2	846	109.2	869	107.7
815	111.1	858	108.4	861	108.2
822	110.8	868	107.8	845	109.3
831	110.4	874	107.5		
843	109.4				

Table 9.

Surface tension of castor oil and sodium chloride at different temperatures.

A positive temperature coefficient is such an unusual feature that it was doubted at first whether it was a real effect due to the nature of the slag or a function of the apparatus. High viscosity of the slag for example might mean that with the raising of the temperature the more fluid slag might tend to creep further up the walls of the cylinder and so give a higher reading. Any viscosity effect should be dependent on time however and it was found that a higher surface tension was always obtained at high temperatures even though the cylinder was allowed to remain in the maximum pull position for upwards of one hour at the lower temperatures. In fact, this only gave a reading about 0.1 dyne/cm. lower than the instantaneous reading. Evidently the viscosity effect is that the cylinder picks up slightly too much liquid which requires time to form its equilibrium surface contour. It should also be noted that molten glasses, much more viscous than slags, have given negative temperature coefficients using this method (see Babcock[5]).

Further confirmation that the apparatus can reveal negative coefficients was obtained by measuring the surface tension of castor oil over a range of 50°C. A negative coefficient was obtained. The results for molten sodium chloride also show a negative coefficient. (See Table 9.).

It was concluded therefore that the positive coefficient obtained with rhodonite was in fact a property of the slag. Perhaps the best proof is that a calcium aluminate slag does show a negative coefficient, though it has a viscosity similar to that of rhodonite.

In the following account one or two minor points of experimental procedure are noted.

Fluidity of Slags.

The more fluid slags give more accurate readings and better reproducibility of results. (See p.47). All the manganese silicates, iron silicate and most of the ternary slags give reproducible readings without much difficulty. The magnesium silicate slag does not seem to be reasonably fluid below 1550°C. The scatter of results makes it necessary to adopt a mean value for the temperature coefficient which is not so accurate as those of the preceding slags. The same difficulty was experienced in a lesser degree with the calcium metasilicate and calcium aluminium silicates.

Atmosphere Control.

All the slags except the manganese and iron silicates can be melted in air. An atmosphere of purified nitrogen was used for the manganese silicates, though the

admission of air did not seem to alter the surface tension appreciably. The iron silicate presented problems not met with in any of the other slags. An atmosphere of purified nitrogen, mixed with a little hydrogen was employed, but this is only partly successful in preventing oxidation, as is shown by a 9% Fe_2O_3 content of the melt. The slag was soaked just above its melting point while surface tension measurements were made. These increased with time, presumably due to pick-up of iron from the crucible, but eventually reached a steady value. Raising the temperature, however, resulted in further pick-up of iron. Because of this, the slag was heated to 1470°C. and allowed to soak for some time. Readings were then taken as the slag cooled. According to Kozakevitch[4] these slags do not pick-up iron further when cooled from high temperatures. The hysteresis effect cannot be shown on this slag and the temperature coefficient quoted in Table 3. is that obtained on cooling. The coefficient on heating is listed for all other slags.

Cleaning of Crucibles.

The more basic slags, especially those containing iron and manganese, are readily removed from the crucibles by fusion with sodium and potassium carbonates and subsequent solution of the fusion in acid. It is unsafe to use

hydrochloric acid for manganese slags since a considerable amount of permanganate is formed during fusion which produces chlorine, attacking platinum crucibles. Slags containing magnesia are best removed by inverting the crucible and melting out. Cleaning is a lengthy process for acid slags and tends also to shorten the life of the crucibles.

Colour of Slags.

Manganese, magnesium and iron silicates and calcium aluminate crystallise quite readily. The other slags, especially the more acid compositions, tend to give glasses. In some cases the colour is of interest. Calcium aluminate for example gives a grey slag from two white components. Calcium aluminium silicates show a slight yellow tinge; magnesium silicate is white but addition of alumina produces a bluish opalescence. Calcium silicates are all white. Of the manganese silicates, rhodonite is definitely pink, while tephroite has the greenish tinge of MnO.

Part VI.

Structure of Liquid Slags.

Some discussion on the subject of liquid slag structures is necessary to appreciate the hypothesis developed in Part VII to explain certain features of the experimental results.

For many years the structure of the liquid slag has been inferred from the examination of solidified melts. There has arisen a picture of the liquid slag as consisting of oxides and silicate compounds, partly dissociated so that both free and combined oxides are present. It is perhaps not true that this picture has been literally accepted everywhere but the equilibrium relations between slag and metal in the open-hearth furnace can normally be satisfactorily treated on such an assumption[36]. A convenient model has thus come to be pictured as a reality.

Two advances in the state of knowledge have modified this view considerably. Firstly, the general theory of the liquid state has progressed to such an extent that a qualitative picture of different liquid structures can be readily drawn. The advances in this domain are well summarised in recent publications[37].

Secondly, it has been realised that liquid slags are quite analagous to glasses[38]. Glasses lend themselves

more readily to investigation since they show, in the solid state, the structure of the supercooled liquid. Largely due to the work of Zachariasen[39] and Warren[40] the structure of glasses is now well understood. This correspondence between slags and glasses must have been appreciated earlier by Herasymenko[41] and Martin and Derge[42], who have recognised that slags are also truly ionic substances.

Work on critical phenomena has for long tended to emphasise the similarity betweenthe liquid and gaseous states. It is likely, however, that a liquid, just above its melting temperature, and therefore far removed from its critical temperature, bears more resemblance to the solid structure. The, truth of this hypothesis can be inferred from the fact that liquids differ only slightly from their crystalline solids in density and specific heat. The molecular pattern in the liquid state must then be quite similar to that in the solid state except for some change which occurs abruptly at the melting temperature. This change requires very much less energy than the change to the gaseous state, as is indicated by the difference between the heats of melting and vaporisation. It is natural to expect that the change brought about by melting is the loss of the long-range order which characterises the crystalline state.

Short-range order is, however, preserved as is indicated e.g. by the X-ray work of Warren[40] on molten glasses. Discrete $(SiO_4)^{4-}$ tetrahedra were observed in the melts and these are the units of the solid structure. Thus, the difference between the solid and liquid states is not fundamental but lies only in the degree of order and particularly that of long-range order. The liquid possesses the same structural units as the solid but the regularity of structure extends over smaller distances and each unit is not possessed of the same symmetry.

This close correspondence between the liquid and solid states is more easily appreciated in the case of glasses for these show no sharp melting point nor does the solid possess the degree of long-range order characterised by the crystalline state. Many glasses can, however, crystallise on annealing; the crystalline structure is preserved to some extent in the glass structure which is, in turn, very similar to the liquid structure.

There is, therefore, no sharp distinction between slag minerals which normally exist as glasses in the solid state and those which crystallise. Both types produce liquids which preserve the characteristics of the solid state but the glass-forming minerals are likely to show a closer resemblance between solid and liquid.

The structure of liquid slag minerals can therefore be visualised in a qualitative manner if the structure of the solid is known; the picture thus obtained is clarified further by the greater knowledge of similar glass structures.

The structures of solid silicates are well known through the work of Bragg[43] and others. They are all typically ionic structures, the Si - O bond being about 50% ionic and that between added metal ions and oxygen more ionic still e.g. the Mg - O bond is 75% ionic. Since the co-ordination number of silicon is four, each silicon ion in the structure is surrounded by four oxygen ions in tetrahedral configuration. Most of the added metal ions show co-ordination numbers of six, though aluminium, for example, can appear in four co-ordination and thus replace silicon. The silicate structures are best regarded as built up of units of $(SiO_4)^{4-}$ tetrahedra with the other metal ions in the interstices of the structure. These tetrahedra share only corners, never faces or edges, since otherwise the repulsion between the powerful silicon ions at small distances of approach would render the structure unstable. The complexity of the silicate structure is then determined by how many of the four corners of each tetrahedron are shared with other tetrahedra. The simplest silicate ion is the discrete tetrahedron $(SiO_4)^{4-}$

with all four corners unshared, the so-called island structure. This is found in the orthosilicates, $2MO.SiO_2$. The tetrahedra are linked by metal ions bonded to the unshared oxygen ions. When tetrahedra share one or two corners silicate ions such as $(Si_2O_7)^{6-}$, $(Si_3O_9)^{6-}$ or more complex group structures are obtained. Sharing of two corners can also mean that endless chains are formed, e.g. the pyroxenes, to which class belong the metasilicates $MO.SiO_2$. The silicate ion can only be given the formula $(n.SiO_3)^{2n-}$ since no discrete $(SiO_3)^{2-}$ groups exist. Sheet or layer structures in which three corners of each tetrahedron are shared are found in mica and talc; these have a closed hexagonal network of six tetrahedra extended as an infinite sheet and represented by the radical $(Si_2O_5)^{2-}$. The feldspars show the framework or network structure which is also characteristic of silica itself. All four corners of the tetrahedra are shared with others. Since this may be done in three ways there are three crystalline modifications of solid silica.

Any binary silicate system can be regarded as the addition of metal oxide to silica with a resulting modification of the initially complex silica structure. This is a discontinuous process if crystalline solids

are formed as the equilibrium diagrams for binary silicate systems show. Silicate compounds and eutectics only are formed, e.g. the sodium silicate system shows three compounds with eutectics between silica and the disilicate, between the disilicate and metasilicate and between the metasilicate and the orthosilicate. The silicate ions present become less complicated as the compounds contain more sodium oxide.

The structure of any liquid composition or glass can be predicted from the above solid structures. Silica glass is known to possess the same extended network as crystalline silica except that the network is irregular and lacks periodicity. Liquid silica therefore should have the same type of structure, in which the degree of long-range order is very small. It must be expected that the network is not quite continuous, as in crystalline silica.

Commercial glasses and slags contain appreciable amounts of other metal cations. The effect on a silica glass of adding another cation is to break up the silica network at certain points so that the added cation can be accommodated in the structure in co-ordination with oxygen ions. Only those oxygen ions which are bonded to one silicon ion are available for co-ordination with an added

cation hence the network must be disrupted.

This break-up is responsible for the pronounced effect of alkalis in lowering the viscosity of silica glass melts.

Break-up of the network is only complete at the orthosilicate composition, where the solid must consist of discrete silicate tetrahedra sharing no corners. It is significant that soda glasses cannot be formed with more soda than the orthosilicate composition; glass-forming oxides must, according to Zachariasen[39] possess a network type of structure. Glass of metasilicate composition will possess a structure in which the network is broken up to an intermediate extent.

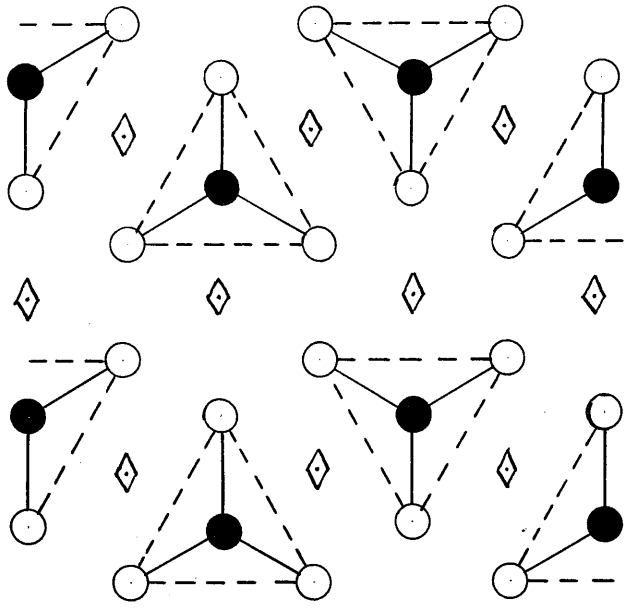
It is not quite certain that the added cation is distributed uniformly throughout the network structure. In a low soda content glass for example, there may be regions where the network is largely split up to the extent demanded by the metasilicate composition adjacent to regions consisting substantially of silica[44].

The added ion also attempts to co-ordinate with its proper number of oxygen ions. Since the silicon ion has a high field strength it tends to retain oxygen ions and the tetrahedral co-ordination of oxygens round silicon is

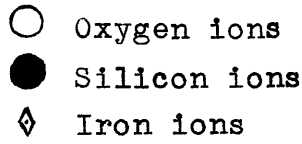
preserved in glasses. Full co-ordination for the added ion is not possible without the network being considerably split up. Unless the added ion has a considerable field strength, however, it can be accommodated in the holes in the network with a lower co-ordination than Pauling's rules decree, e.g. the alkalis which form glasses very readily.

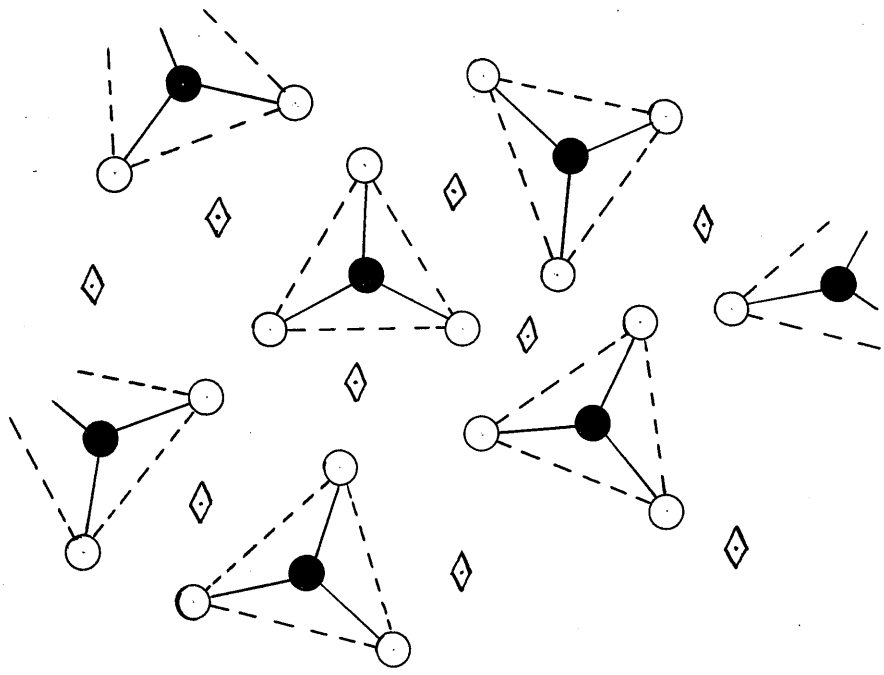
The cations of higher field strength, e.g. calcium, magnesium, manganese and iron, which are present in slags, cannot be added to silica in small amounts without the production of two phases, as is evidenced by the immiscibility region in the equilibrium diagrams. (A tendency to immiscibility is revealed also by the S-shaped melting curve in the soda-silica system). One phase is almost pure silica, the other contains an appreciable amount of metal oxide, so that there is sufficient oxygen to enable both silicon and other cations to exist in the structure with the desired co-ordination. The glass forming tendency and the tendency to form compounds are also very much less with these cations of higher field strength than with the alkalis.

This general theory of the structure of glasses, which is very much strengthened by the experimental work of Warren and Biscoe[45] has been very successful in explaining the viscosity[46], density[47] refractivity[48] and colour[49] of glasses.



Solid.





Liquid.

Fig. 8.
Two-dimensional representation of structure of fayalite.
(after Richardson.)

The same reasoning can be applied to the structure of slag minerals, which, in the liquid state, and at temperatures not far removed from their melting points, are quite analagous to glasses. The important differences are:-

1. Slags contain much higher percentages of added cation; therefore the silica network structure is so split up that the glass forming tendency is small.

2. The added cations, e.g. Mg^{2+}, Mn^{2+}, Fe^{2+}, Ca^{2+} have higher field strengths than the alkalis customary in commercial glasses; therefore the silicon ion suffers greater competition in attaining its full co-ordination with the available oxygen ions.

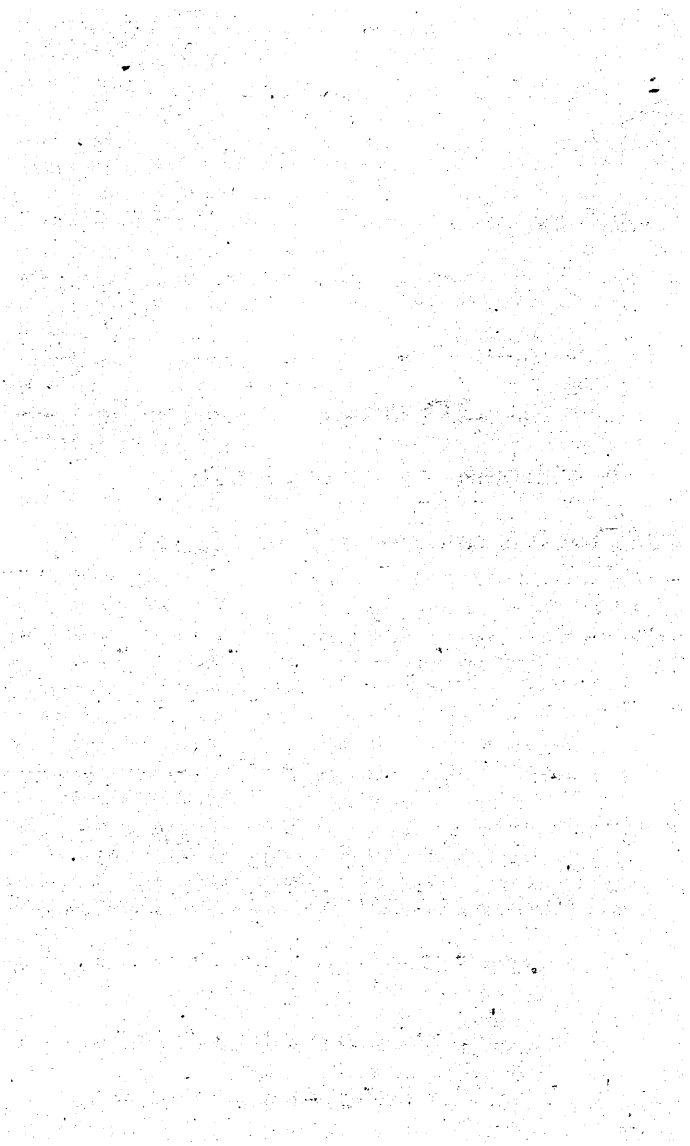
Richardson[3] and Bockris[38] have given definite expression to this view of liquid slags. Richardson regards liquid fayalite, an orthosilicate, as similar to the solid structure. The ions present in the liquid are then $(SiO_4)^{4-}$, the discrete silicate tetrahedra, and Fe^{2+} ions the only difference from the solid being in the degree of order. (See fig. 8.)

Metasilicate slags should, in the liquid state, possess essentially the chain-like structure of the solid.

The silicate ions are then $(nSiO_3)^{2n-}$. In the liquid it is likely that the chains become irregular, of finite length and perhaps give way to group structures in some places. This structure must be imagined to be constantly breaking up and reforming. At any given instant then, there will be areas where the $(SiO_4)^{4-}$ type of ion predominates and areas where the network characteristic of liquid silica is the predominant structure. These areas will constantly change in size and position but, in sufficiently fluid melts, will tend to approximate to one structure type at any single temperature.

The slags examined in this investigation have compositions varying from the orthosilicate to the metasilicate. All, therefore, possess structures in which the silicate ions are less complex than the network groupings characteristic of glasses. The structures vary in complexity from the separate silicate tetrahedra found in the orthosilicates to the chain or ring structures found in metasilicate compositions. Intermediate compositions may be expected to have a mixed type of structure in which separate tetrahedra co-exist with rings or chains. Compositions slightly higher in silica than the metasilicate composition will, by analogy, possess a few network remnants

in conjunction with rings and chains.



Part VII.

Discussion of Results I

Positive Temperature Coefficient.

A positive temperature coefficient of surface tension is a most unusual feature, yet all the slags investigated, with two exceptions, show an increase of surface tension with temperature. Such positive coefficients have been reported previously; for example, mercury is often described as behaving in this way, though the likely explanation in this case is that oxide films, which are dissociated at higher temperatures, are responsible. Certain organic liquids do have positive temperature coefficients. Recently, Shartsis, Spinner and Smock[50] have shown that fused lead oxide, boric oxide, some lead borates and lead silicates have positive temperature coefficients. Other positive coefficients are reported for glasses high in lead oxide and barium oxide by Shartsis and Smock[51].

Where any attempt has been made to explain the effect it has been attributed, rather loosely, to the presence of associated molecules in the liquid. This would give the observed result, since the associated molecules tend to break-down to simpler types at higher temperatures. Thus, more unsatisfied bonds are available in any small area of the liquid surface; therefore the surface energy increases. This effect might well be larger than the

reduction in surface tension brought about by thermal expansion. Such an explanation seems feasible in some cases but benzene, for example, is known to be associated yet shows a negative temperature coefficient of surface tension. In this case, however, the lowering of surface tension due to thermal expansion may be larger than the raising due to dissociation of the complex structure.

Some phenomenon comparable to association must be responsible for the anomalous behaviour of the present series of slags.

The present results have served to strengthen a view which was put forward tentatively by King[18] on the basis of results obtained only on a rhodonite slag. According to this view, the known instability of rhodonite, reflected in its incongruent melting point, and because of its proximity to that higher silica region of the manganese oxide - silica equilibrium diagram which shows immiscibility, is responsible for a tendency, which can be satisfied in the liquid state, towards breakdown into tephroite and silica according to the equation:

$$2(MnO.SiO_2) \rightleftharpoons 2MnO.SiO_2 + SiO_2$$

The breakdown should be facilitated at higher temperatures.

In the liquid state the replacement of the chain structure remnants of rhodonite by the island structure characterised by tephroite is the same type of phenomenon as that which takes place in the breakdown of an associated structure and should therefore lead to an increased surface tension. The effect is larger than the decrease produced by thermal expansion alone.

A similar, more detailed, hypothesis has been put forward by Towers[52] to explain anomalous viscosities in the manganese silicates.

It is worth while to consider this suggested breakdown more fully in order to appreciate just why it should lead to an increase in surface tension. The chemical equation given is misleading in that it suggests a picture of the molten state in which molecular tephroite co-exists with silica and unaltered molecular rhodonite. The discussion in Part VI shows that such a picture is a convenient model rather than a true representation of the liquid. However, even with this picture, it is possible to see that the replacement, in any small surface area, of rhodonite by tephroite and silica (in which the degree of order is not highly enough developed for it to be considered as another phase) should lead to an increase in surface

tension. The surface tension of rhodonite at the lowest temperature measured, i.e. 1450°C., is 410.8 dynes/cm. At 1580°C. the surface tension has risen to 415.8 dynes/cm. Replacement of two structural units of rhodonite by tephroite and silica units in the small surface area considered means that units of 410.8 dynes/cm. are replaced by one of 492 dynes/cm. and one of 340 dynes/cm. (The value for silica is taken from Dietzel[53] and is obtained from considerations of the surface tension of many glasses).

Hence the expected average for these units is 416.0 dynes/cm., an increase of 5.2 dynes/cm. over that of the rhodonite units. This increase is more than sufficient to account for the observed increase of 5.0 dynes/cm.

The argument is, of course, speculative; the surface tension of mixtures may not be the average value. Also, the value used for rhodonite is that of a structure which has already broken down to an unknown extent on melting and up to the lowest temperature measured. The contrary effect of thermal expansion cannot be estimated. Hence, predictions from these results as to the degree of breakdown of the rhodonite structure that does actually take place are quite uncertain. The silica-rich groupings are also likely to have a higher surface energy than that of pure silica.

This hypothesis, that with increase in temperature rhodonite tends to breakdown into tephroite and silica rich groupings, is supported by the results for all the other slags examined. The original hypothesis is, however, developed in greater detail and made applicable in a more general manner to all types of slag in the following paragraphs. Confirmatory evidence, from work on the electrical conductivity of slags and the properties of synthetic glasses, is also discussed.

In the development of this broader view of the explanation for the anomalous temperature coefficient of surface tension, the model of the liquid slag structure postulated in Part VI will be used. This ionic model is a truer representation of the liquid structure than the molecular picture which has been inferred above.

According to the ionic model, the solid structure of rhodonite, (which is of the pyroxene type, in which long chains of silicate ions of composition $(n.SiO_3)^{2n-}$ are bound together by linked Mn^{2+} ions,) is substantially retained in the liquid state. However, since only short-range order is possessed, the chains in the liquid cannot be infinite in length. Remnants of the long chains, with links constantly breaking and reforming due to heat motion,

exist, in conjunction with manganese ions which will be attached, on the average, to those units of the chain structure which contain oxygen ions unshared with other silicon ions.

Break down of these chains will mean that greater co-ordination of the manganese ions with oxygen ions is possible, since oxygen ions which were shared between two silicon ions are now singly shared and can co-ordinate with manganese ions.

A certain amount of breakdown of this type must occur when the crystalline solid melts. The chain remnants can be of any length, dependent on the range over which order is present, in turn dependent on temperature. The lower limit of length is the silicate tetrahedron $(SiO_4)^{4-}$. Groupings such as $(Si_3O_9)^{6-}$, intermediate between the chain and tetrahedron, are also likely to be present due to the breakdown, but it must not be thought that there is any rigid pattern in the structure, which is constantly changing in any one area and also, at any time, varying from place to place in the liquid.

It is suggested that, at higher temperatures, the striving of the manganese ions for full co-ordination with oxygen ions and the general tendency towards greater

randomness result in further breakdown of the chain structure, i.e. the complex silicate ions tend to give way to simpler types such as $(SiO_4)^{4-}$. The composition is such that the areas containing Mn^{2+} and $(SiO_4)^{4-}$ groups must be equal in number to areas containing groups of the pure silica type, i.e. fragments of the silica network present in glasses, or complexes such as $(Si_2O_5)^{2-}$. Some manganese ions may, however, be loosely co-ordinated with these groups to offset the tendency towards separation into two liquid phases.

Since, as the results for the four manganese silicates show (see Table 3), the surface tension increases regularly as the percentage of Mn^{2+} ions in the slag increases, then the appearance of these groups in the rhodonite structure which are characteristic of silicates higher in manganese oxide, results in an increase of the surface tension. This increase must be larger than the decrease due to thermal expansion, consequent upon the rise in temperature. Hence, a positive temperature coefficient is observed.

The phenomenon may be compared to that of the dissociation of a structure composed of associated molecules. The more complex silicate ions, of the chain

or ring type are broken down, as the temperature rises, into simpler ions of the island type. It is interesting, in this connection, that Dietzel[53] believes the relatively low surface tension of fused silica to be due to the grouping of the silicon ions in a network structure, which gives much the same effect as any other associated liquid.

The driving force for the breakdown of the complicated silicate anions is the lack of full co-ordination between the powerful Mn^{2+} ions and O^{2-} ions. At higher temperatures the manganese ions find it easier to attract oxygen ions to themselves and so attain fuller co-ordination.

The breakdown process may be pictured in equations (which, however, give the false impression that the structure is uniform over large areas) as follows:-

$$n(MnO.SiO_2) \overset{\text{on melting}}{\rightleftharpoons} n.Mn^{2+} + (n.SiO_3)^{2n-}$$

$$n.Mn^{2+} + (n.SiO_3)^{2n-} \overset{\text{as temp. is raised}}{\rightleftharpoons} nMn^{2+} + \frac{1}{2}n(SiO_4)^{4-} + \frac{1}{2}(n.SiO_2)$$

It is impossible to say just how far the breakdown process goes, i.e. whether many remnants of the chain-type ions $(n.SiO_3)^{2n-}$ remain in the liquid, at the highest temperature recorded. The possibility also arises that some free oxygen ions are present, i.e. some of the groups $(SiO_4)^{4-}$ breakdown as follows:-

$$(SiO_4)^{4-} \rightleftharpoons (SiO_2) + 2O^{2-}$$

The latter statement is prompted by the result for the manganese orthosilicate, which already possesses the island type of structure, even in the solid state, yet still shows a small positive temperature coefficient of surface tension. This question is further discussed on p. 83.

The hypothesis demands that the liquid slag structure be not uniform. In all cases, to mantain the composition proportions, the breakdown of each complicated anion must give rise to a simpler ion and also to silica-rich network groupings which co-exist in the same phase. The manganese ions are mainly associated with the simpler silicate anions formed for, there, better co-ordination with oxygen is possible. Hence, the other areas of the structure are relatively poor in manganese ions. There is a similarity between this picture and that of the group structure theory of glasses which is discussed later (see p.92).

Note.

Fig. 9. (overleaf) in which are plotted some of the results listed in Tables 3 to 8, is included to illustrate the points brought out in the following sub-sections. These deal with (1) Variation of positive coefficient with silica content, and (2) Variation of positive coefficient with different cations.

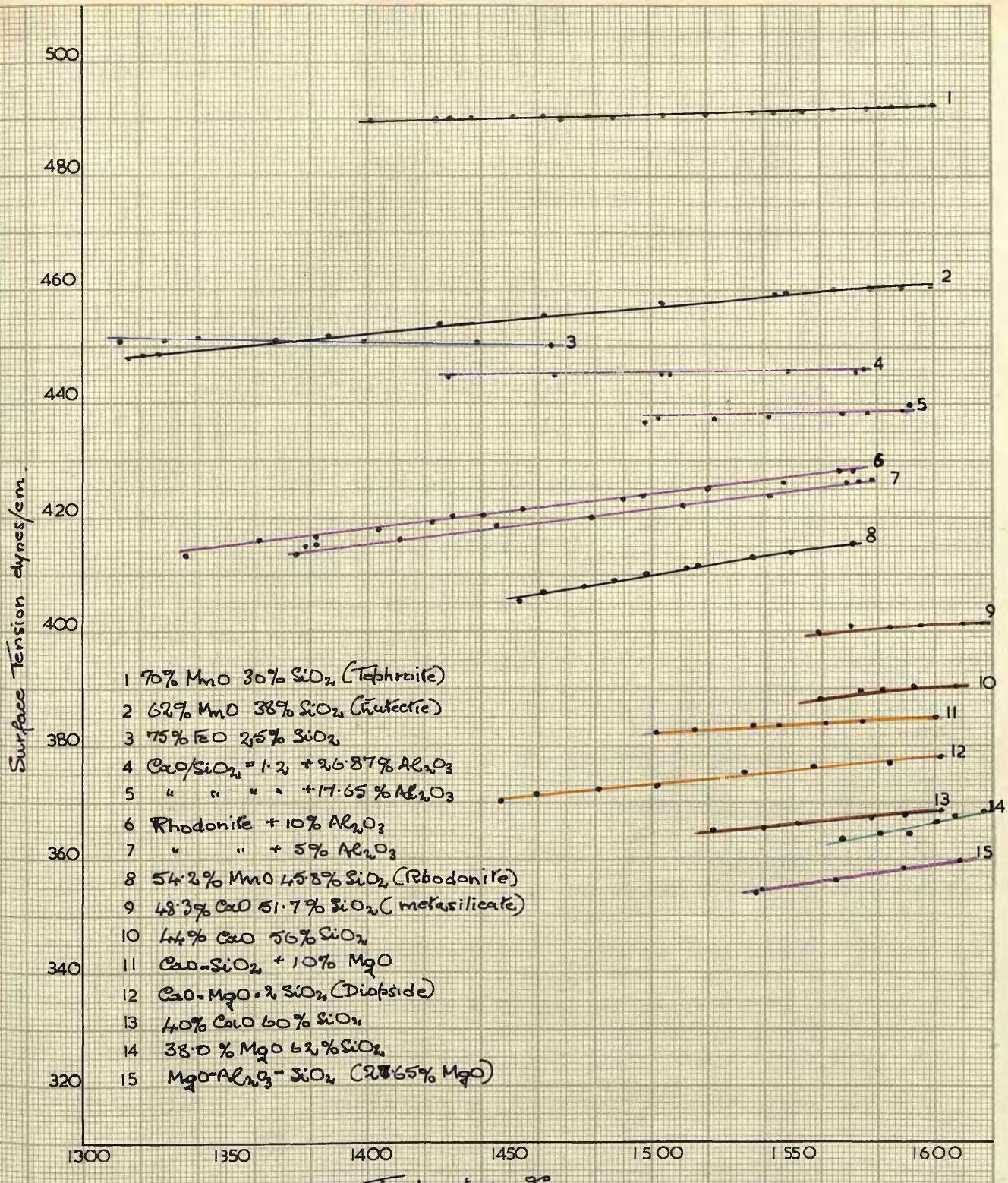


Fig. 9.

Surface tension v. Temperature.

Variation of positive temperature coefficient with silica content.

In Part V it was shown that increasing the basic oxide content and decreasing the silica content in a binary system, e.g. $MnO-SiO_2$ and $CaO-SiO_2$, decreased the value of the temperature coefficient of surface tension. On the hypothesis outlined this is a result which would be expected. Probably two effects combine to make the behaviour of slags high in basic oxide more normal.

In the first place the initial liquid structure formed on melting is less complex at low silica contents. There already exists a larger proportion of simple silicate ions such as $(SiO_4)^{4-}$ in the melt and therefore there are fewer complex ions of the ring or chain type. Any breakdown of the structure which is liable to take place at higher temperatures is therefore likely to be of small extent and also to be completed at temperatures not too far above the melting point. Thus, a manganese silicate of the eutectic composition shows a small positive coefficient which is visibly decreasing at higher temperatures (see Fig. 6).

Secondly, the higher oxygen content of such melts means that the co-ordination of the cations can be more fully achieved, so that there is less tendency towards disruption

of the structure.

It is not at first obvious why an orthosilicate, e.g. tephroite, should show a slight increase of surface tension with temperature. The structure formed on melting contains only discrete silicate tetrahedra, hence, any further breakdown must result in the production of free oxygen ions and corresponding silica rich groups. It is possible that the attraction of Mn^{2+} ions for oxygen is sufficiently strong to bring this about. Rey[54] believes that, while weak cations like Na^{+} cannot remove oxygen completely from silicon, stronger cations, e.g. Fe^{2+} and Mn^{2+} can; melts from the latter cations then contain free oxygen ions. The greenish colour of tephroite also supports this view.

A different explanation is enrichment of silica on the surface of the melt, which must take place, since silica lowers the surface tension of all the basic oxides studied. This enrichment must be small (see p.103) but is nevertheless sufficient to make a melt which is of the orthosilicate composition in the interior, higher in silica on the surface. The surface, then, will contain a few silicate ions more complicated than the $(SiO_4)^{4-}$ type

and therefore be capable of breakdown. Both processes may contribute to the result.

Compositions richer in basic oxide than the orthosilicate should, on the present hypothesis, show a negative temperature coefficient of surface tension. This is the case for the 75% FeO, iron silicate. (See Table 3).

Support is lent to this deduction by the observation of Kozakevitch[4] that the viscosity of slags varying from pure FeO to iron orthosilicate is low and is practically constant, but further silica additions cause a rapid rise in viscosity. The conclusion is that anions more complicated than the separate tetrahedra only appear in liquid compositions higher in silica than the orthosilicate.

Element	Ionic Valency Z	Ionic (C.N.6)$_o$ Radius r in A	Common Co-ord'n No. (C.N.)	M-O Distance a.	Field Strength Z/a^2
K	1	1.33	8	2.77	0.13
Na	1	0.98	6	2.30	0.19
Ba	2	1.43	8	2.86	0.24
Ca	2	1.06	8	2.48	0.33
Mn	2	0.91	6	2.23	0.40
Fe	2	0.83	6	2.15	0.43
Mg	2	0.78	6	2.10	0.45
Al	3	0.57	6 4	1.89 1.77	0.84 0.96
Si	4	0.39	4	1.60	1.57

Table 10.

Arrangement of Cations according to Field Strength.

Variation of Positive Temperature Coefficient with Different Cations.

The discussion in Part V has revealed that the value of the temperature coefficient of surface tension is related to the basic oxide which is present in the silicate melt. Manganese orthosilicate shows, for example a positive coefficient of the same order as calcium metasilicate though the effect of silica content on the coefficient is much the same in both systems. The order of increasing temperature coefficient for the same molar silica content, has been shown (p.54) to be Ca, Mn, Mg.

In Table 10 the ionic radii of some cations are given. The radii increase in the order Mg, Mn, Ca. While the ionic radius is a criterion of the strength of the ion it can only be applied to ions of the same valency, for example the sodium ion is smaller than the barium ion but is also weaker. A better criterion is the field strength of the cation. This is expressed in Table 10 as the valency over the square of the interionic distance M-O. It is a guide to the strength of the bond between the cation and oxygen ions. The field strength expressed in this way increases in the same order as the positive temperature coefficient, as is shown below.

Cation	Field Strength	Temp.coeff.of surface tension dynes/cm/°C.
Ca	0.33	0.021
Mn	0.40	0.086
Mg	0.45	0.098

This is a result which would be expected on the hypothesis outlined. According to this, the driving force for breakdown of silicate ions into simpler types is the lack of full co-ordination between the cation and oxygen. This must be dependent on the attractive force for oxygen which the cation exerts, i.e. on the field strength of the cation. Weaker cations such as calcium can be accommodated in a homogeneous structure with a smaller oxygen co-ordination than the powerful magnesium ions. These are strong enough to attract oxygen ions from silicon, thereby achieving fuller co-ordination. Oxygen ions which were originally bonded to more than one silicon ion are now singly bonded. Thus, complex silicate anions are broken down into simpler types, freeing oxygen ions for co-ordination with magnesium ions.

This structure cannot be homogeneous, as is possible with very weak ions where no breakdown takes place, since the magnesium ions must congregate with simple silicate anions leaving corresponding areas richer in silica.

Though the weakest cation investigated is Ca^{2+} it is possible to make certain deductions concerning the alkali ions Na^{+} and K^{+} which are of such importance in glasses. Calcium metasilicate shows only a very small positive temperature coefficient. The alkalis are much weaker ions and can therefore be accommodated in a complex silicate structure with lower co-ordination than calcium ions, as is evidenced by the fact that there is no immiscibility region in their equilibrium diagrams. It is likely, therefore, that these silicates behave normally with respect to temperature, a conclusion which is verified by the considerable literature on the surface tension of glasses. A search of this has failed to reveal any positive temperature coefficients for alkali glasses, even at high silica contents.

There is an indication in the results set out in Table 3 that the least stable silicate compounds are those which have a large positive temperature coefficient of surface tension. As the equilibrium diagrams reveal, magnesium and manganese metasilicates melt incongruently, whereas, calcium metasilicate melts congruently. Of these silicates, calcium also shows the smallest positive temperature coefficient.

The relation between the temperature coefficient and the stability of compounds can be translated into a relation between the field strength of the ion and the stability of compounds. (See p. 90). As is also pointed out later (p. 90) tephroite is unusual in having a very small positive coefficient yet possessing an incongruent melting point.

Dietzel[55] has related the stability of compounds to the volume change on melting, which is also an indication of the degree of breakdown of structure. His results show that the volume change is less for calcium than for magnesium metasilicate.

Related Phenomena.

The hypothesis which serves to explain the anomalous surface tension results is supported by work which has been carried out on certain related phenomena. These are briefly discussed in this section to emphasise the similarity between the explanations advanced by other workers and that given here.

Immiscibility in Binary Systems.

Kracek[56] has shown that the appearance of immiscibility in binary silicate systems is related to the strength of the cation. There is no immiscibility in the alkali silicates and the immiscibility gap extends to higher concentrations of basic oxide as the strength of the cation increases, up to 43% FeO in the iron silicate system. Warren[57] explains the appearance of immiscibility as being due to the demands of the cation for singly bonded oxygen ions which are too few in number at high silica contents to allow a single phase to be present. Two liquid phases result, one almost pure silica, the other containing most of the basic oxide. The attraction of the alkali ions for oxygen is supposed to be small enough to enable them to fit into the structure without full co-ordination.

Immiscibility is thus a stage further in the

"heterogeneity" brought about by the breakdown postulated in Part VII. Rey[54] has also shown that the number and stability of silicate compounds is smaller in those systems which contain cations of high field strength. Alkali silicates show compounds up to the trisilicate, the number decreasing in other systems, as the immiscibility gap spreads, until only one compound, the orthosilicate, is present in the iron silicate system; even this compound is not particularly stable, as the flat melting curve reveals. It is of passing interest that tephroite is unusual in having an incongruent melting point, this diagram may need revision.

Viscosity.

Endell and others have made a systematic investigation of the viscosities of silicates. Endell[58] has been able to explain the variation of viscosity in these binary systems by considering that high viscosity is associated with complex silicate ions. Thus, the viscosity falls rapidly as additions of basic oxide break up the silica network. The viscosity also decreases as the field strength of the cation increases. This is to be expected on the present hypothesis, since simpler silicate anions are present in melts containing ions of higher field strength.

It is also notable that the viscosity of acid open-hearth slags is generally greater than that of basic

slags but decreases much more rapidly as the temperature increases (see Towers[52]). This is perhaps explained by the greater breakdown of structure which is possible in the acid slags.

Electrical conductivity.

Bockris and his co-workers have recently determined electrical conductivities of simple slag systems[38]. The conductivity is high enough to make it certain that slags are completely ionic liquids. Manganese silicates have higher conductivities than calcium silicates. This is explained as being due to the higher field strength of the manganese ions which results in a looser attraction between manganese and silicate ions. The manganese ions are thus able to move more freely through the silicate structure. Conduction being cationic, a higher conductivity results.

It is easier to visualise the process as the movement of manganese ions through a structure which is broken down to a simpler type than in the calcium silicate.

Anomalous Viscosity.

Perhaps the most interesting results are those obtained by Towers and Kay[52] on the viscosities of manganese silicates. They showed that the viscosity of rhodonite

was dependent on the rate of shear, being smaller at high rates of shear. Rhodonite is thus a non-Newtonian liquid. This behaviour was less noticeable at higher temperatures. Towers and Kay attributed the anomaly to the tendency for the chain structure of rhodonite to break down under shear into an island structure, characteristic of tephroite, with associated silica groupings. The explanation is thus the same as that advanced here for the anomalous surface tension results, but it is interesting that shear can evidently bring about the same type of breakdown as takes place with increasing temperature. The effect falls off at high temperatures because the degree of dissociation has been advanced by temperature so that there is less breakdown to be brought about by shear. No anomalous effect is noticeable with slags higher in manganese oxide than rhodonite but that the effect does still exist is apparent from the present surface tension results.

Group Structures in Glasses.

While it is generally conceded that glass structures are based on the silica network with added cations it is not universally accepted that these cations are distributed uniformly throughout the network with low oxygen co-ordination. Warren's results[40] for example do

not prove that the distribution is uniform.

Preston[59] has advanced a theory of glass structure in which glasses up to 34%Na_2O are considered to be "heterogeneous", being made up of a mutual solution of silica and sodium disilicate. Glasses containing more than 34% Na_2O are supposed also to contain areas of sodium metasilicate composition.

O'Daniel[60] has taken this idea of inhomogeneity further in a theory which states that all possible structure elements, pyrosilicate, disilicate or more complex groups are built into the silica network.

Dietzel[55] has advanced views similar to those of Preston but has extended the theory to other cations. Glasses containing soda are supposed to consist of areas of disilicate, or, at higher soda contents, metasilicate, co-existing with silica network groupings. With calcium silicate, metasilicate groupings only exist since there is no disilicate formed. Dietzel also believes that magnesium silicate is broken down on melting so that orthosilicate groupings are present in the melt.

The similarity of these views to those advanced here is obvious. All these workers have found no difficulty

in picturing the melt as inhomogeneous insofar as different structure elements can co-exist in small areas within one liquid phase. In the present work, the field strength of the cation is given a more prominent place in determining whether or not a given melt will be "heterogeneous;" it is also recognised that more basic melts tend to greater homogeneity.

Effect of Alumina.

The effect of alumina on the temperature coefficient of surface tension is of interest, since the aluminium ion is of comparable field strength with silicon and is known to be capable of replacing silicon in tetrahedral configuration with oxygen. Aluminium can thus appear in either four or six co-ordination. Which co-ordination is adopted seems to depend mainly on the strength of the other cations present. In the presence of strong cations, e.g. in Al_2O_3, six co-ordination is favoured. Replacement of silicon in silicates by aluminium leaves the surrounding four oxygen atoms each with a $\frac{5}{4}$ residual valency instead of 1. This must be satisfied by additional cations. Thus, the introduction of aluminium into slags should enable the cations to co-ordinate with oxygen with less breakdown of the silicate structure. This does seem to happen with

those slags to which alumina has been added; a slight diminuition in the temperature coefficient is produced. The same process is probably responsible for the disappearance of the immiscibility region in binary silicates when alumina is added.

The normal behaviour of the calcium aluminate slag is an indication that aluminates are quite unlike silicates, though the aluminium ions exist entirely in four co-ordination with oxygen. Evidently there is not the same tendency to form complex anions as in the case of the silicates. There is no immiscibility region in the CaO-Al_2O_3 system so that both calcium and aluminium ions are able to achieve the desired co-ordination with oxygen in a homogeneous melt. The structures should therefore be reasonably stable in the molten state. The very high value of the surface tension of this aluminate is also an indication that alumina does not form the same type of network structure as silica. (Wartenberg[61] quotes the surface tension of molten alumina as 577 $\pm$ 30 dynes/cm. i.e. much higher than silica, although the field strength is lower.)

It is difficult to see how continuous structures can be formed with aluminium in four co-ordination with oxygen, because of valency considerations, unless silicon is also present.

Variation of Temperature Coefficient with Temperature.

It has been shown in Part V that the temperature coefficient becomes smaller at high temperatures for those slags which have a small initial temperature coefficient or in which the melting point is low enough to enable measurements to be continued to a temperature well above the melting point.

At sufficiently high temperatures the surface tension of all the slags must begin to decrease in order that the surface tension should vanish at the critical temperature. The breakdown of structure which is responsible for the increase of surface tension must eventually reach a limit. This could be determined by the complete break-up of the structure of a metasilicate, for example, into the orthosilicate structure and silica. It is unlikely that complete breakup does occur, the tendency for separation into two liquids might become too strong. Rather is it likely that intermediate ion types are also present. The cations can probably achieve a sufficient co-ordination with only a partial breakdown; this is certainly true for the weaker cations such as calcium. Calcium silicates do show a diminishing temperature coefficient at 1600°C. which is not far above their melting points, whereas rhodonite shows no sign of diminuition at this temperature

which is 150°C. above its melting point.

Hysteresis Effects.

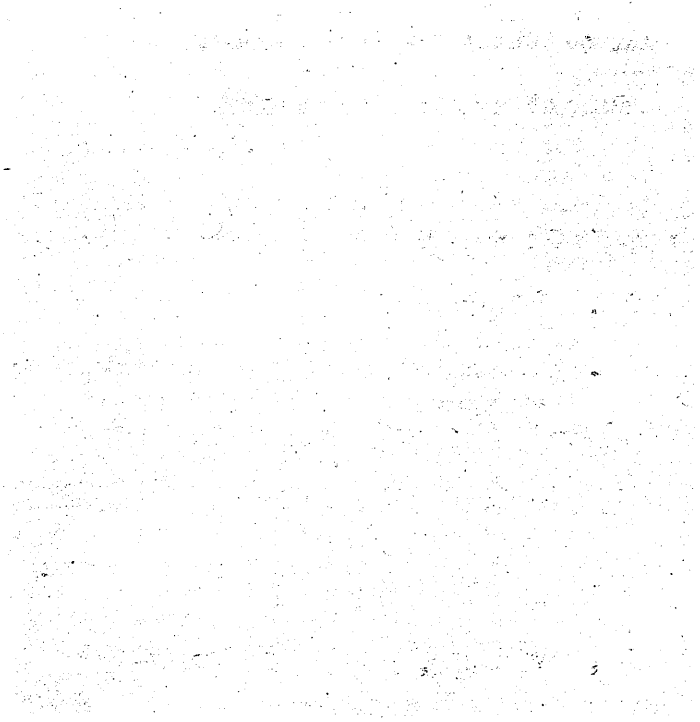
The hysteresis which is noted between measurements taken on heating and cooling (see p. 57) suggests that the breakdown of structure accomplished by raising the temperature is not fully reversible on cooling; the slag tends to remain in the high temperature state.

Bockris and his co-workers[38] noted this same hysteresis in their conductivity work. This was explained as being due to the tendency of the cations on cooling to remain in lower energy wells in the structure which they had reached on heating.

This must mean that a certain activation energy, supplied by temperature fluctuations, is necessary for breakdown of the silicate structure. Restoration of the system is therefore more difficult to accomplish at lower temperatures where the effect of thermal fluctuations is less.

It should be noted, however, that Towers and Kay[52] obtained the same value of viscosity when the shearing rate was initially large and allowed to fall to the value measured and when it was on the measured value

from the beginning. This would indicate that the postulated breakdown is instantaneously reversible. The comparison is not a strict one however, since the conditions governing breakdown by shear are not necessarily those governing breakdown by temperature.



Part VIII.

Discussion of Results II

Surface Tension Values.

Slag Composition (by wt.)	Surface Tension dymes/cm.	
	Calculated	Observed
40.0% CaO 60.0% SiO_2	391.0	367.0
CaO.SiO_2 ratio + 17.65% Al_2O_3	442.3	438.8
20.3% MgO 61.4% SiO_2 18.3% Al_2O_3	417.5	329.0
27.65% MgO 55.56% SiO_2 16.64% Al_2O_3	428.4	356.8
38.0% MgO 62% SiO_2	414	363.0

Table 11.

Calculated and observed values of surface tension.

The range of compositions studied has not been wide enough to enable many definite conclusions to be drawn from the values of the surface tension. Attention has been centred on the temperature coefficient. However, in view of the amount of work done on molten glasses, it is of interest to see how the values for slags fit into the general pattern. Slags contain less silica than glasses so that their surface tensions are generally higher.

Lyon [35] has given factors, based on experimental results, for the calculation of the surface tension of glasses from their chemical compositions, though such factors, according to Babcock[5], vary a little with the amount of added oxide. Lyon's results are only applicable to glasses in which the silica:soda ratio exceeds 3.25, though corrections are given for higher alkali contents.

It is perhaps unsafe to apply this data to slags which contain no alkali but the surface tensions of some of the present slags have been calculated by the use of these factors. Table 11 gives the comparison between observed and calculated results. Agreement is reasonably good except for the slags containing magnesia. The calculated results are much too high in this case. This

fact is worthy of comment.

The surface tension of the silicates might be expected to increase as the field strength of the cation increases. Dietzel[53] has classified the results for glasses in this way. The effect of a cation on the surface tension of the glass is shown to be greater as the field strength of the cation increases except for those ions which take part in complex anion formation e.g. aluminium and silicon. When those ions are present in a glass the surface tension is much lower than would be expected from their field strengths.

As the results in Table 11 show, the surface tension of metasilicate slags increases in the order Mg, Ca, Mn. Magnesium is thus in an anomalous position according to its field strength. The obvious explanation is that magnesium is showing similar tendencies to aluminium i.e. it is replacing silicon, in four co-ordination with oxygen, in the complex silicate anion so that its full effect on the value of the surface tension is not observed. Huggins[47] has suggested that magnesium in glasses may be present in four-co-ordination.

All the magnesium ions cannot, of course, be distributed in this way in slags. Some must act as true

cations otherwise the considerable breakdown of structure indicated by the positive temperature coefficient would not take place. In this respect magnesium is unlike aluminium which is also an anion-former but which, in the amounts added to slags, is not likely to be present as a cation.

Surface Tension and Composition.

The variation of surface tension with composition in a binary system may follow different courses. Generally, there is a gradual change from the surface tension of one component to that of the other. If the surface tensions of the two components are similar the curve may go through a minimum[2]. Maxima are sometimes observed, e.g. sulphuric acid and water, but it is rare to find a substance which will raise the surface tension of another by an appreciable amount. Hence, the curve between components of widely dissimilar surface tensions is generally flatter near the component of lower surface tension, rising more steeply near the composition of the other. Considerable lowering of surface tension is quite common. Substances which can bring this about when added in small amounts are said to be surface-active, for example, alcohols and the common frothing agents lower the surface tension of water considerably.

Fig. 10.

Surface tension v. Composition.

The surface tension - composition curve in the binary silicate systems is of the first type, a gradual lowering of the surface tension of the metal oxide by silica. This is revealed by the present results for the parts of the $MnO-SiO_2$ and $CaO-SiO_2$ systems which have been covered. These are plotted in Fig. 10 along with the results for $CaO.SiO_2 - MgO.SiO_2$ and the results of Kozakevitch[4] for the $FeO-SiO_2$ system. Only in the latter system are the melting temperatures low enough to enable measurements to be taken up to the pure oxide composition. If these curves are extrapolated to the composition of pure silica the surface tension obtained is of the order 200 dynes/cm. This is very much lower than the value 340 dynes/cm. obtained from glasses. The immiscibility region in these systems makes it impossible to determine the surface tension - composition curve beyond the metasilicate composition.

Fig. 10 reveals that there is no decided break in the curves at the composition of the compounds. This is in line with conductivity[33] and viscosity[46] results (with the exception of a doubtful result quoted by Preston[62]). The obvious deduction is that these compounds do not exist in the liquid slag. (This view has also been advanced in Part VI).

It is not safe to make this deduction from surface tension results alone, since a compound does not always show a peak in the surface tension - composition curve[2].

Foaming of Slags.

Although the theory of the stability of foams is still not on a completely sound basis it seems to be generally accepted that for a liquid to froth satisfactorily one of two conditions must be met.

1. The surface tension must vary sharply with small composition changes or,
2. the liquid must possess a high surface viscosity.

The slope of the curves in Fig.10 is too small to satisfy the first condition. Silica does lower the surface tension of these basic oxides but the shape of the curve is so small that the excess concentration of silica on the surface must, according to the Gibbs adsorption isotherm, also be very small. It is unlikely therefore that silica concentrates on the surface to such an extent that it has much influence on the surface viscosity. Condition 2. is therefore not satisfied.

Kozakevitch[8] has expressed the view that foaming is due to the high surface viscosity of slags caused by

excess silica in the surface layer. In view of the above remarks it does not seem likely that this is the true explanation. The cause of foaming in slags still remains rather obscure, though further work on surface tension may clarify the position.

Part IX.

Summary and References.

Summary.

1. The adaptation of the ring method of measuring surface tension to work on slags at high temperatures has proved successful. The apparatus developed is capable of measuring the surface tension of the more fluid slags up to 1600°C. with a probable accuracy of 1.0 %. It has been shown that a ring and a cylinder of equal diameter do not give the same result on any liquid. The effect of contact angle on the method is shown to be of importance in some cases, sufficiently so to make the ring method unsuitable for some liquids. High viscosity also makes the method difficult to apply.

2. The surface tension of slags is high and, in many cases, increases with temperature. A hypothesis has been advanced to explain the effect. According to this, slags breakdown with increasing temperature to give a "heterogeneous" liquid phase consisting of regions of simple silicate anions, to which most of the basic cations are attached, and regions approximating to silica network remnants. The extent to which this occurs depends on the silica content and the field strength of the cations present. The liquid structure of slags is thus, in many respects, analagous to that of glasses.

3. Surface tension-composition curves are in line with viscosity-composition and conductivity-composition curves in showing no distinct break at the composition of compounds. The inference is that the compounds do not exist as such in the liquid state.

4. Slags containing magnesia have lower surface tensions than might be expected. It is suggested that some of the magnesium ions replace silicon ions in the complex silicate anions.

5. Foaming of slags is discussed, but the surface tension results, so far, do not seem to be of value in elucidating the problem.

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